Observations of NO_2, total peroxynitrates, total alkyl nitrates, and HNO_3 on the Western Slopes of the Sierra:

Implications for Transport of Nitrates to Lake Tahoe

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March 8, 2004

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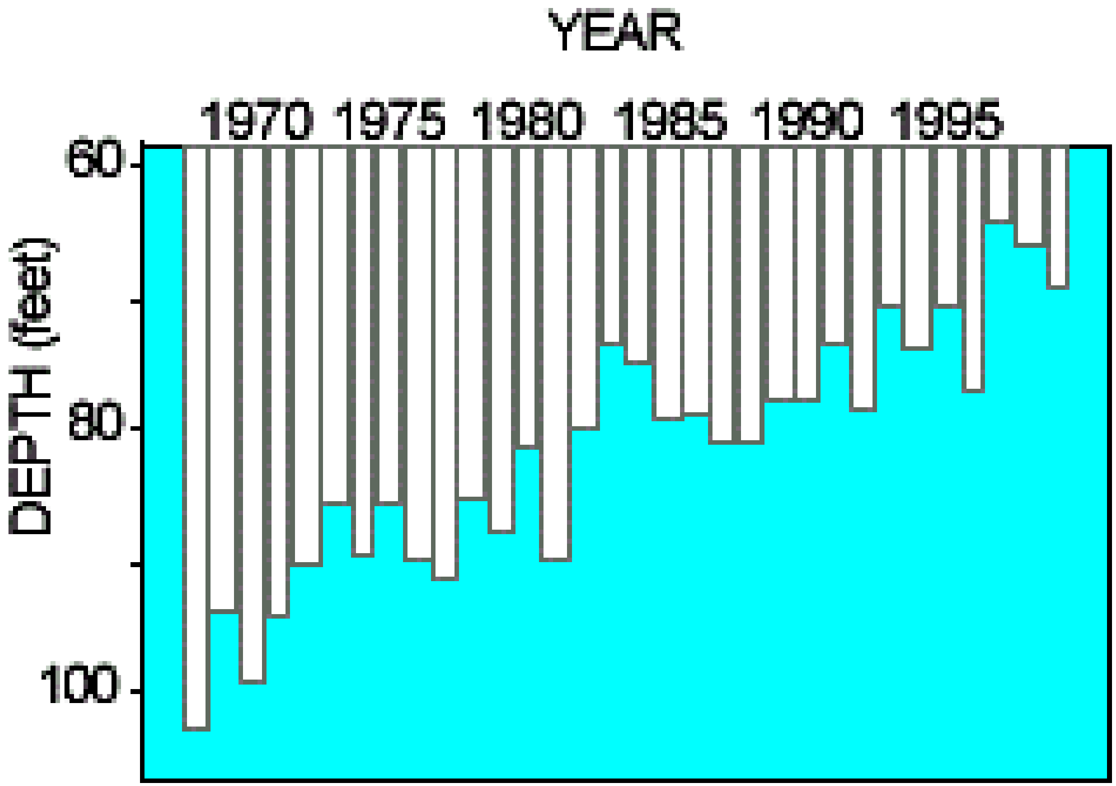
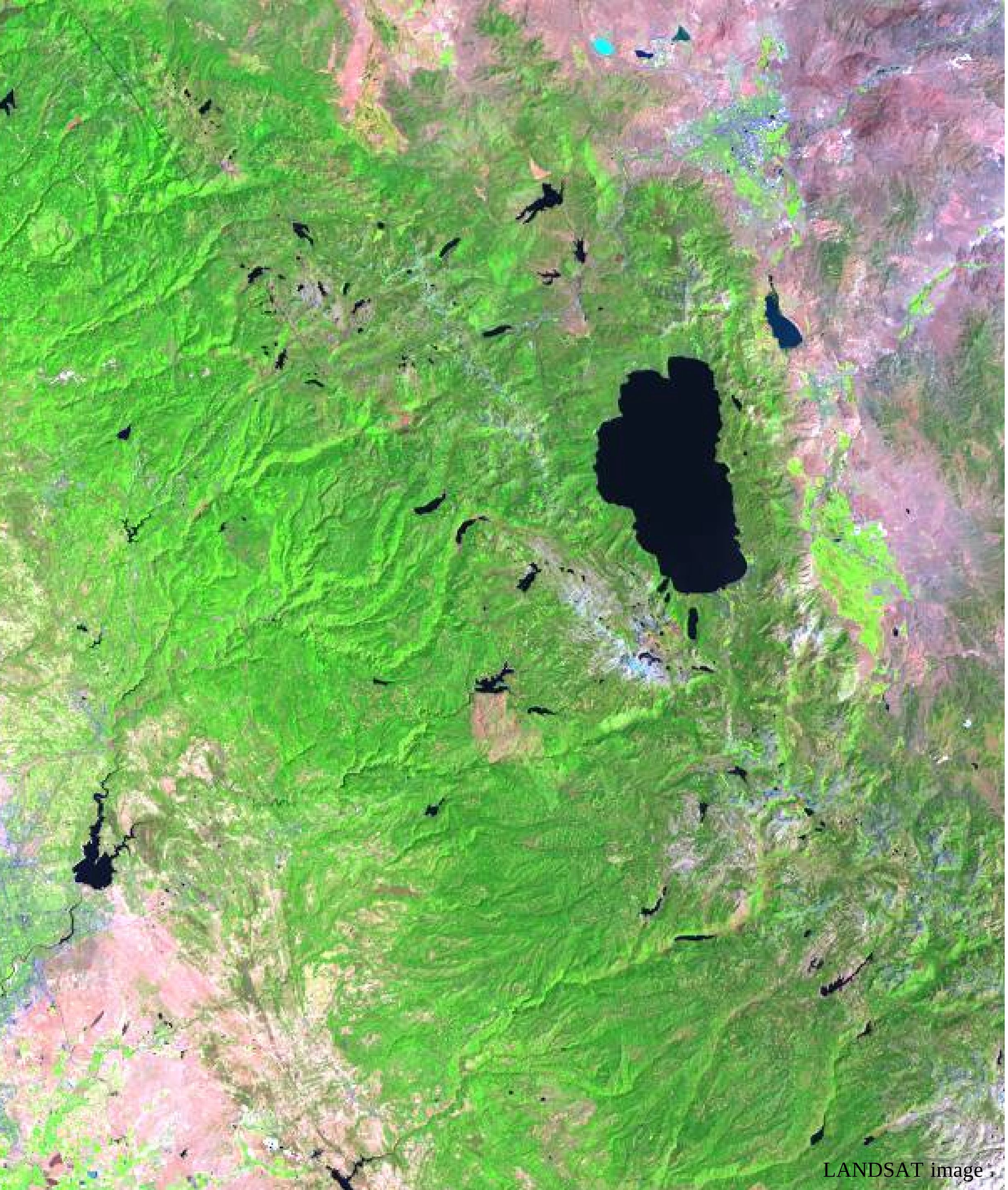
Visibility in Lake Tahoe



The depth at which a white disk can be seen from the surface changes from year to year but generally has become shallower over the decades.

Jassby, et al. TRG UC Davis



- Low natural nutrient concentrations
- Water has a 650 year residence time in the lake
- Visibility decline is due both to algae and mineral particulate
- Nitrogen was the limiting nutrient in 60’s , now phosphorous is


NIGHT
Lake Tahoe
DAY
Sacramento

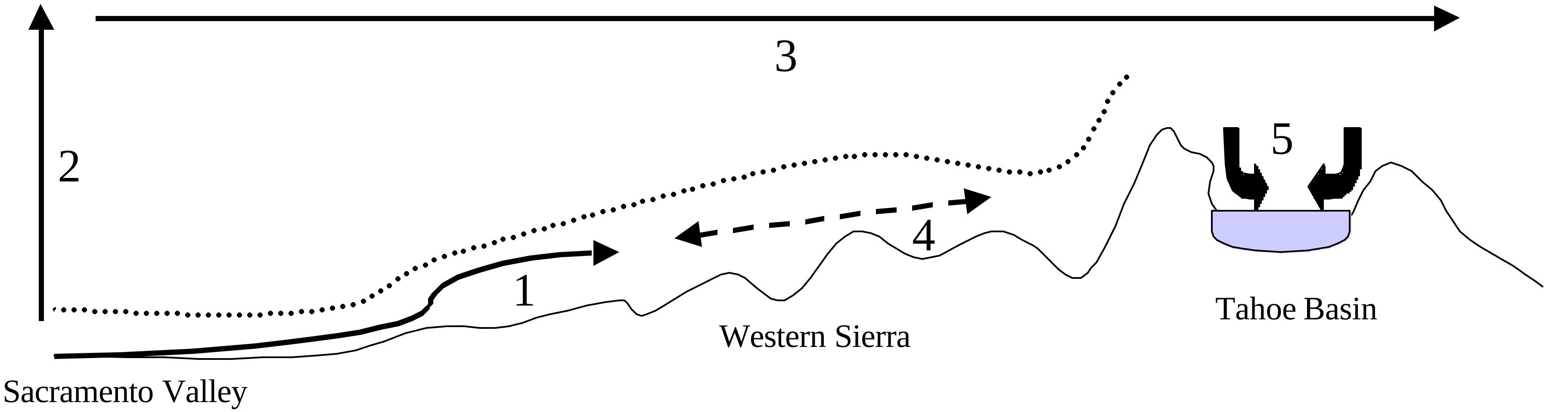
How much of the N that gets to the basin is from west of the basin?

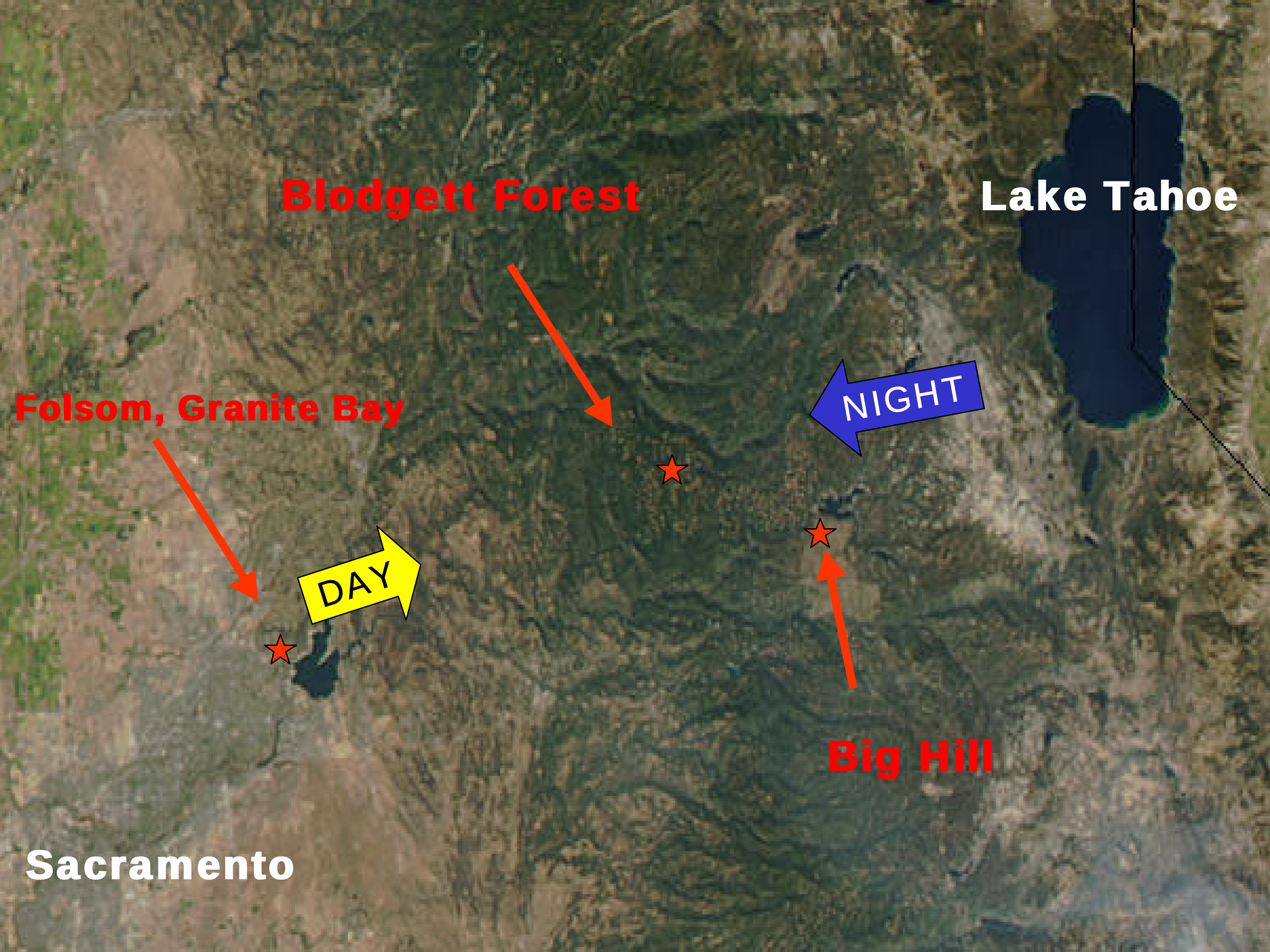
What is a general framework for understanding transport and chemistry within and surrounding the Sacramento plume?

Note: Focus of this talk is on long-term mean—not on extreme events.

Possible transport paths from the West into the Tahoe basin

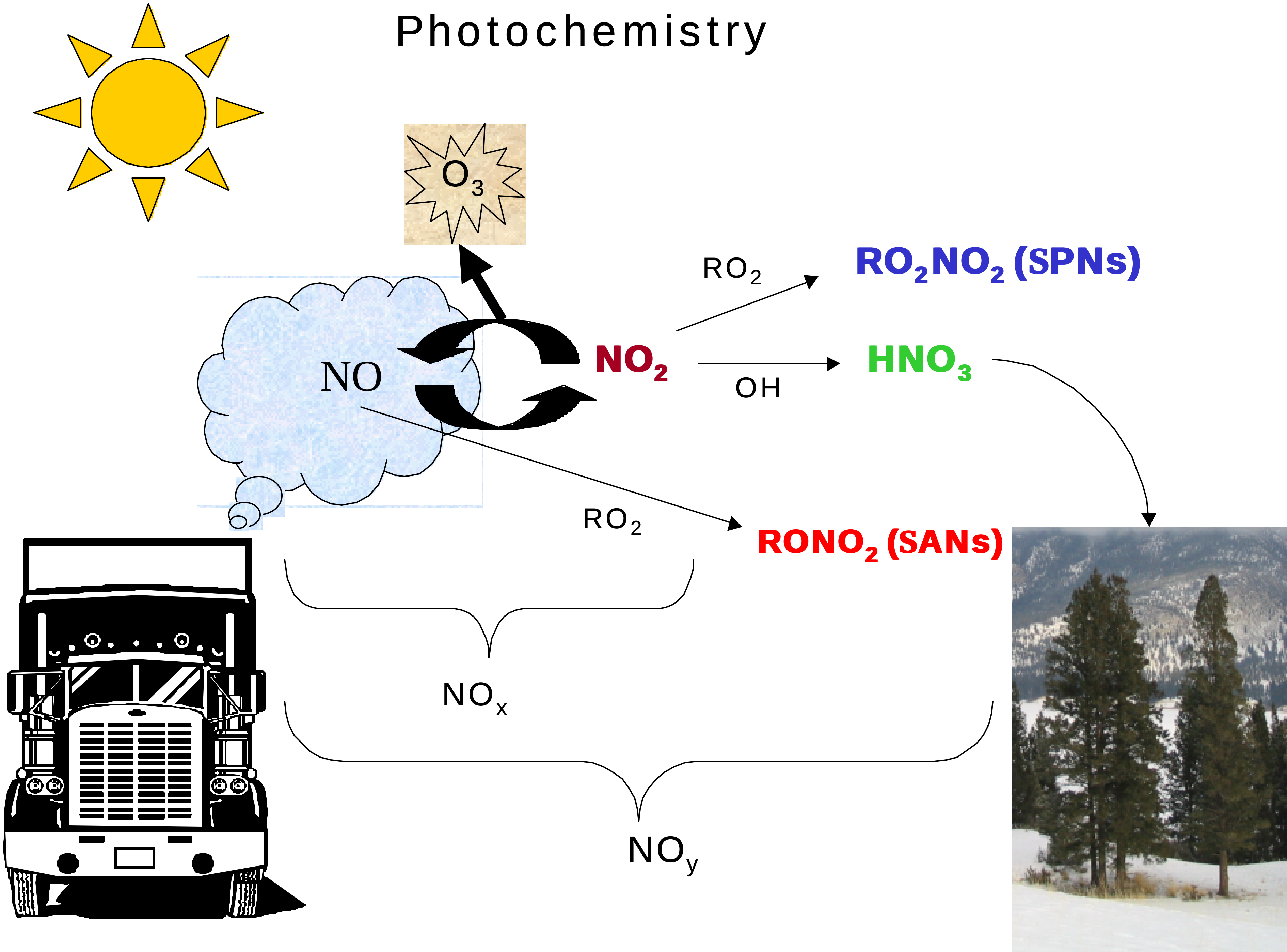
- Advection upslope within the boundary layer
- Vertical Mixing above the boundary layer
- Horizontal transport above the boundary layer
- Recirculation within upslope/downslope boundary layer flows
- Downward mixing within the basin





Blodgett Forest
Lake Tahoe
NIGHT
Folsom, Granite Bay
DAY
Big Hill
Sacramento

Photochemistry



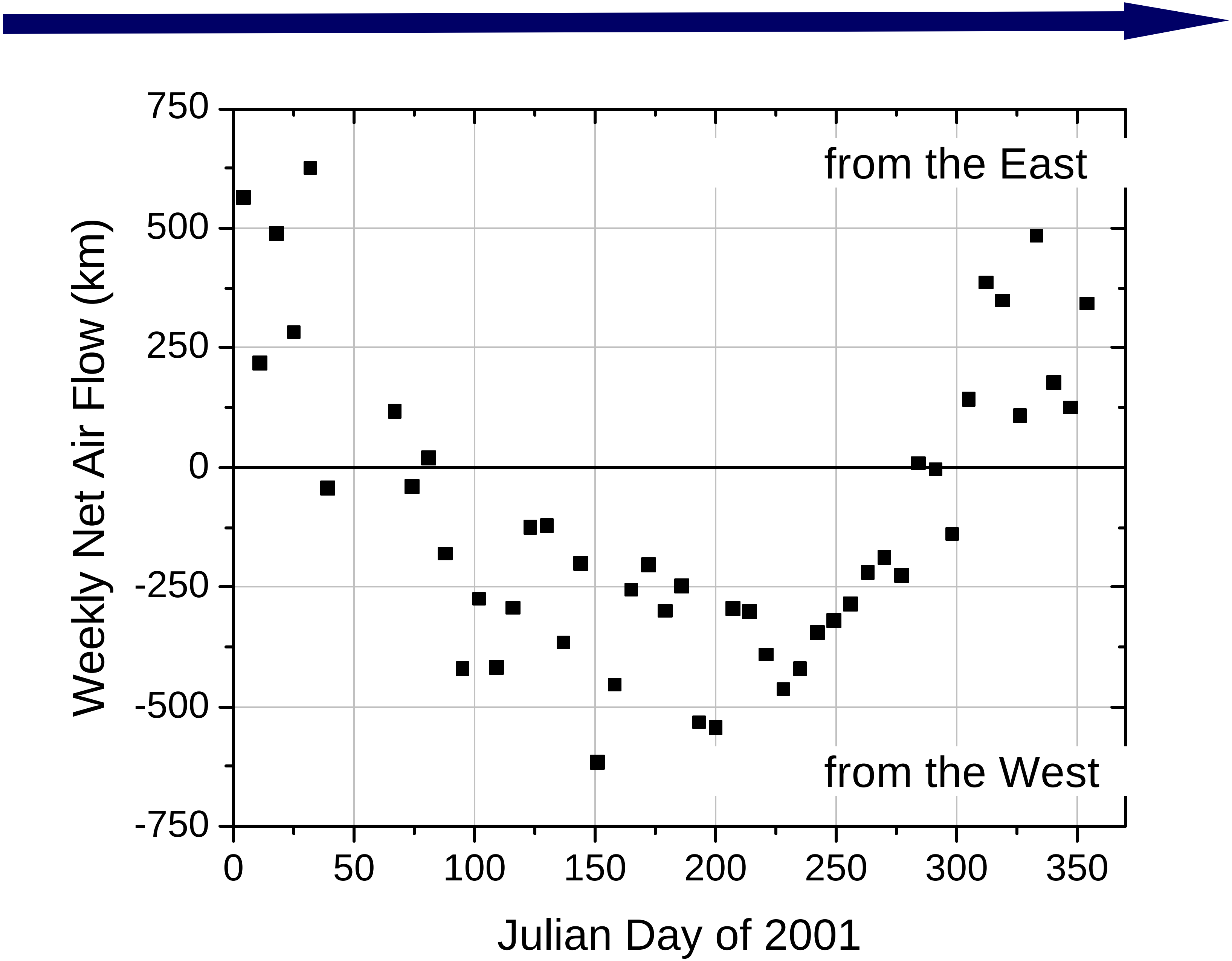
- How far does ‘Sacramento plume’ travel?

- How much dilution and oxidation occurs as the plume moves downwind?

- What do observations of NO_{yi} show?

- Summary and Implications

East-West Net Air Flow at UC-BFRS 2001



- How far does ‘Sacramento plume’ travel?

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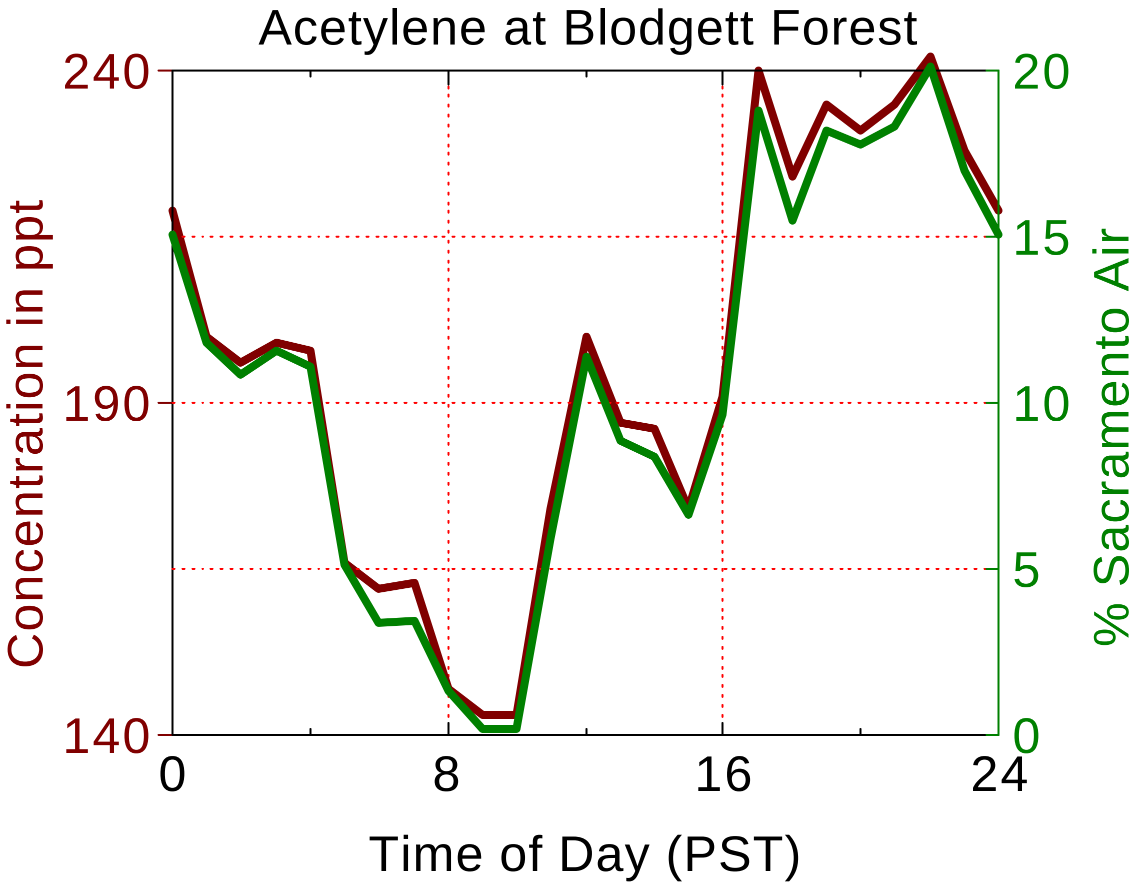
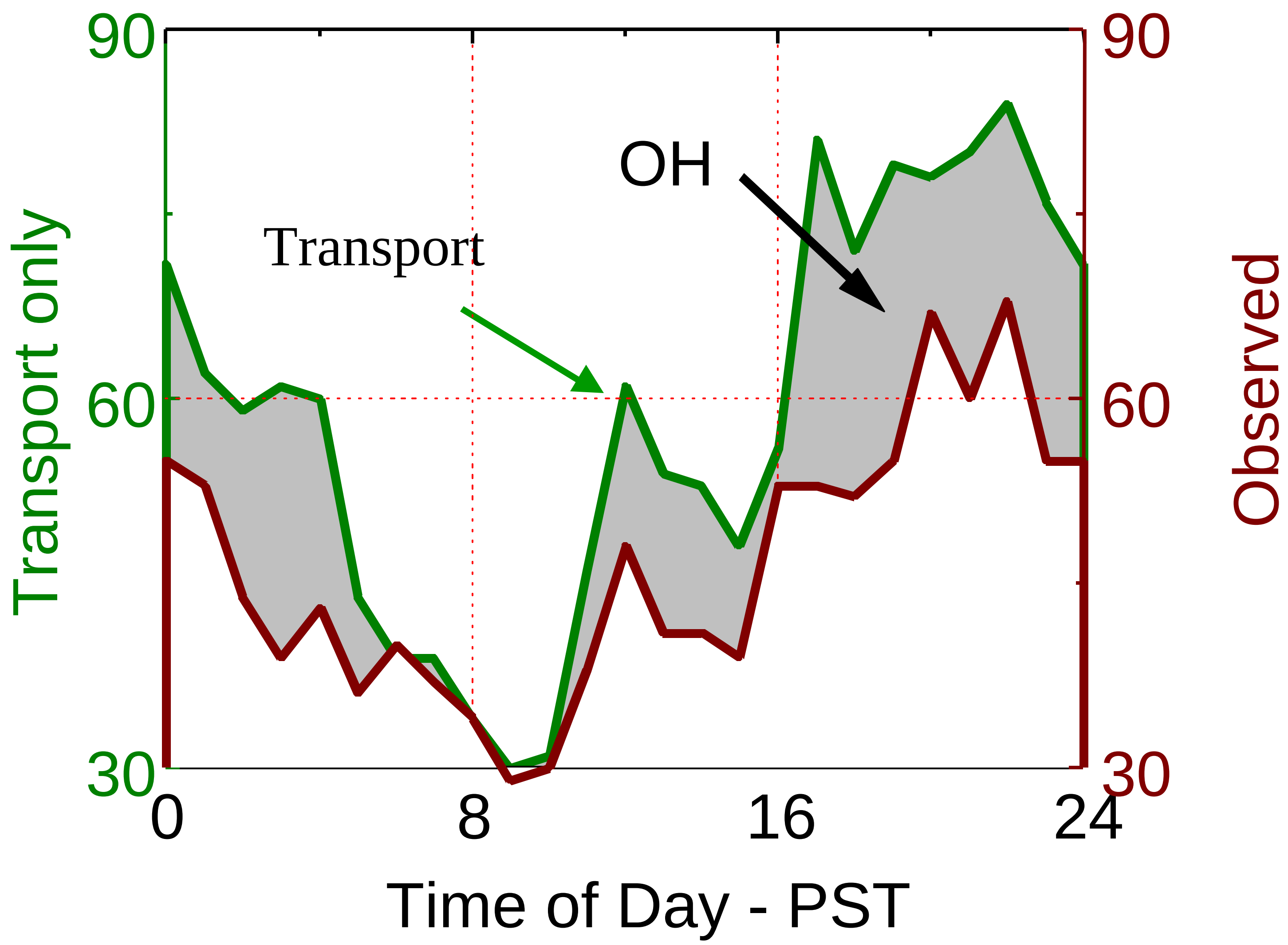
Long-lived hydrocarbons define the fraction of the Sacramento Plume that reaches the foothills



Dillon, Lammana, Schade, Goldstein and Cohen, JGR 107 2002.

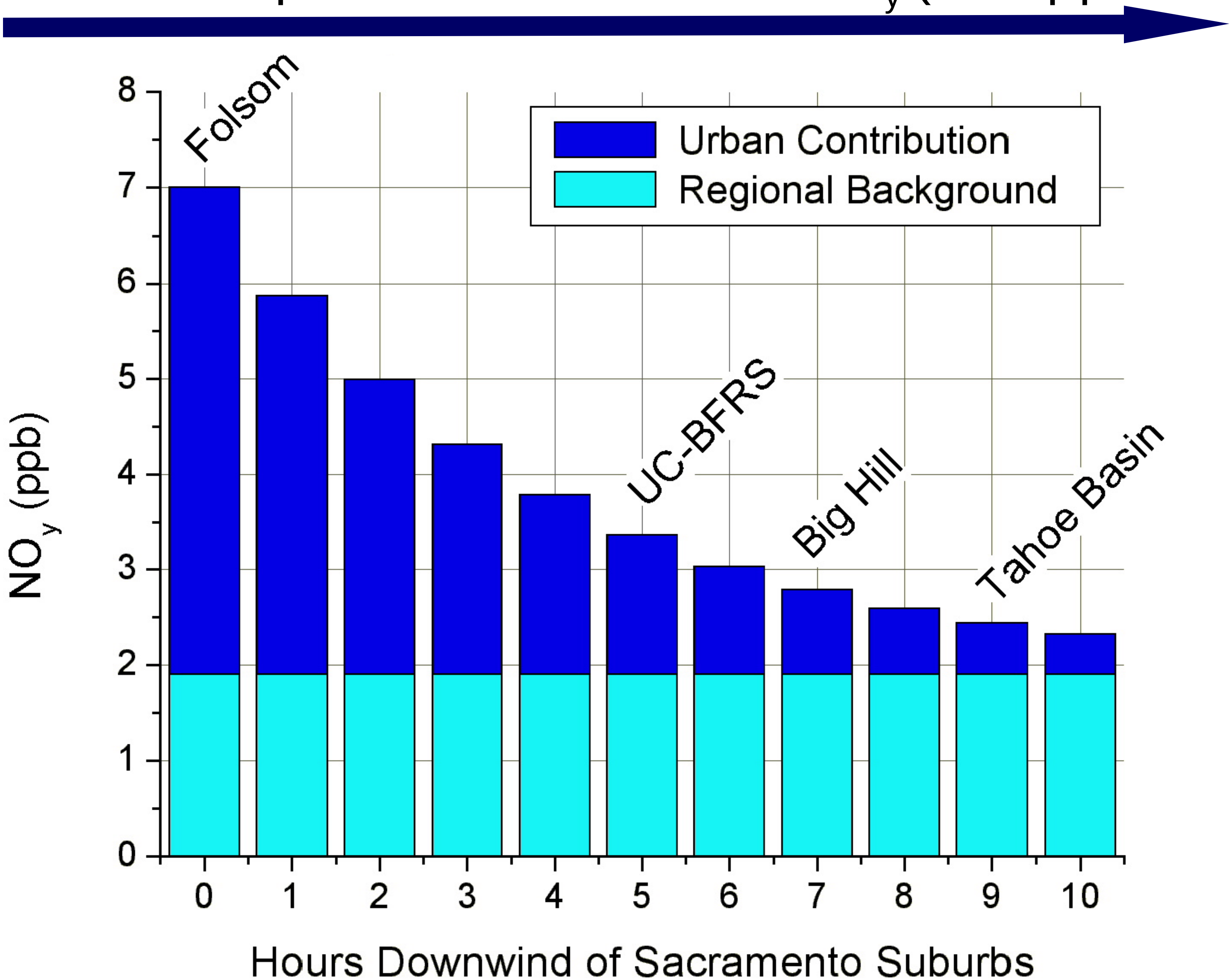
n-Pentane (ppt) at Blodgett Forest - July 1997



Key results

- The Sacramento plume can be accurately described with a model representing advection into the foothills, dilution into the regional background and oxidation.
- The lifetime (e-folding time) with respect to dilution is 4 hours.
- An OH concentration of order 1-1.4x10^7 molecules/cm^3 describes the oxidation that occurs during plume transport.

Pure transport contribution to NO_y (an upper limit)



Implications for NO_{yi}

- We have a good first order model of the amount of NO_y that could be arriving from the west to the foothills of the Sierra (and perhaps as far east as Tahoe).

- The lifetime (e-folding time) with respect to dilution is 4 hours.

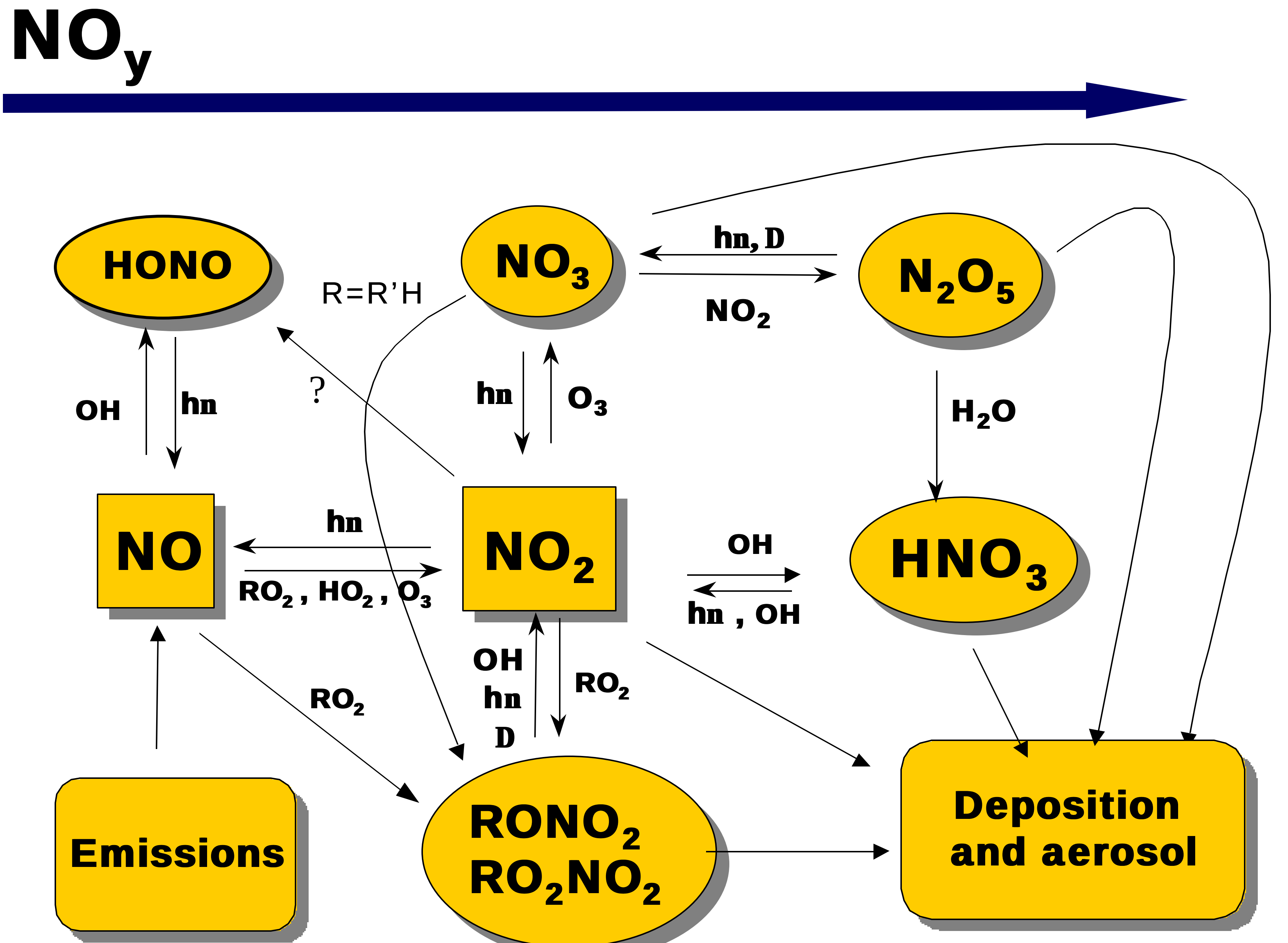
- Oxidation converts most of the NO_2 present in Sacramento and its suburbs to HNO_3, PANs and $RONO_2$ on the same time scale.

- How far does ‘Sacramento plume’ travel?

- How much dilution and oxidation occurs as the plume moves downwind?

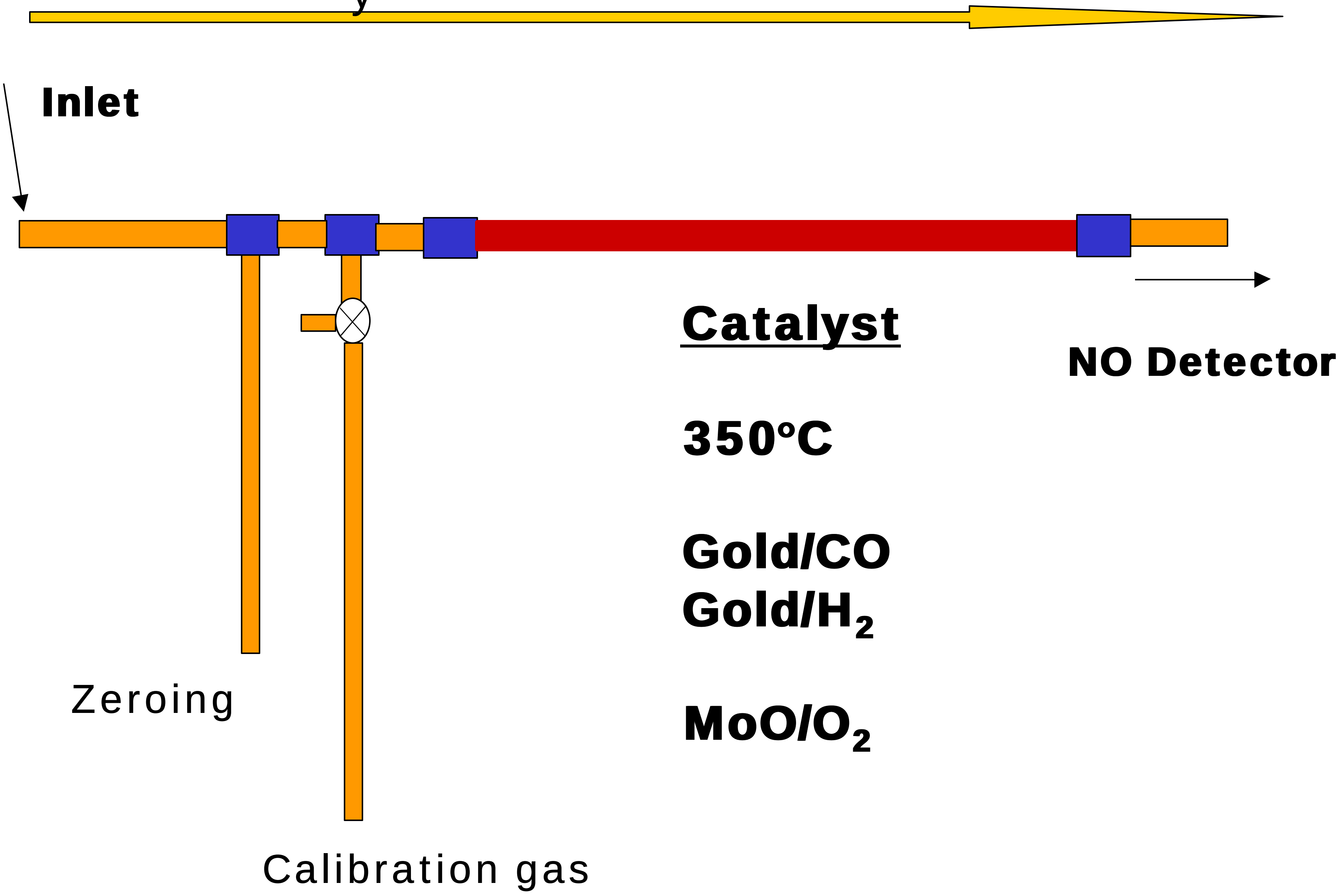
- What do observations of NO_{yi} show?

- Summary and Implications?



NO_y
HONO
NO_3
N_2O_5
R=R'H
hn, D
NO_2
?
OH
hn
hn
O_3
H_2O
NO
NO_2
HNO_3
hn
RO_2 , HO_2 , O_3
OH
hn , OH
OH
hn
D
RO_2
RO_2
Emissions
$RONO_2$
RO_2NO_2
Deposition
and aerosol

Total NO_y Measurements



NO_x measurements with catalyst

- **The catalyst always converts NO_2 and some other stuff to NO.**

- **Typically accurate at the source and in urban areas during the night. Factors of two or more are not unusual at midday in urban areas (for example overestimates of NO_x e.g. 2ppb vs. 1ppb at noon are typical results from field comparisons) .**

- **Usually assume an overestimate of daytime NO_x but an underestimate of daytime NO_y.**

LIF NO_2

Pulsed Dye laser

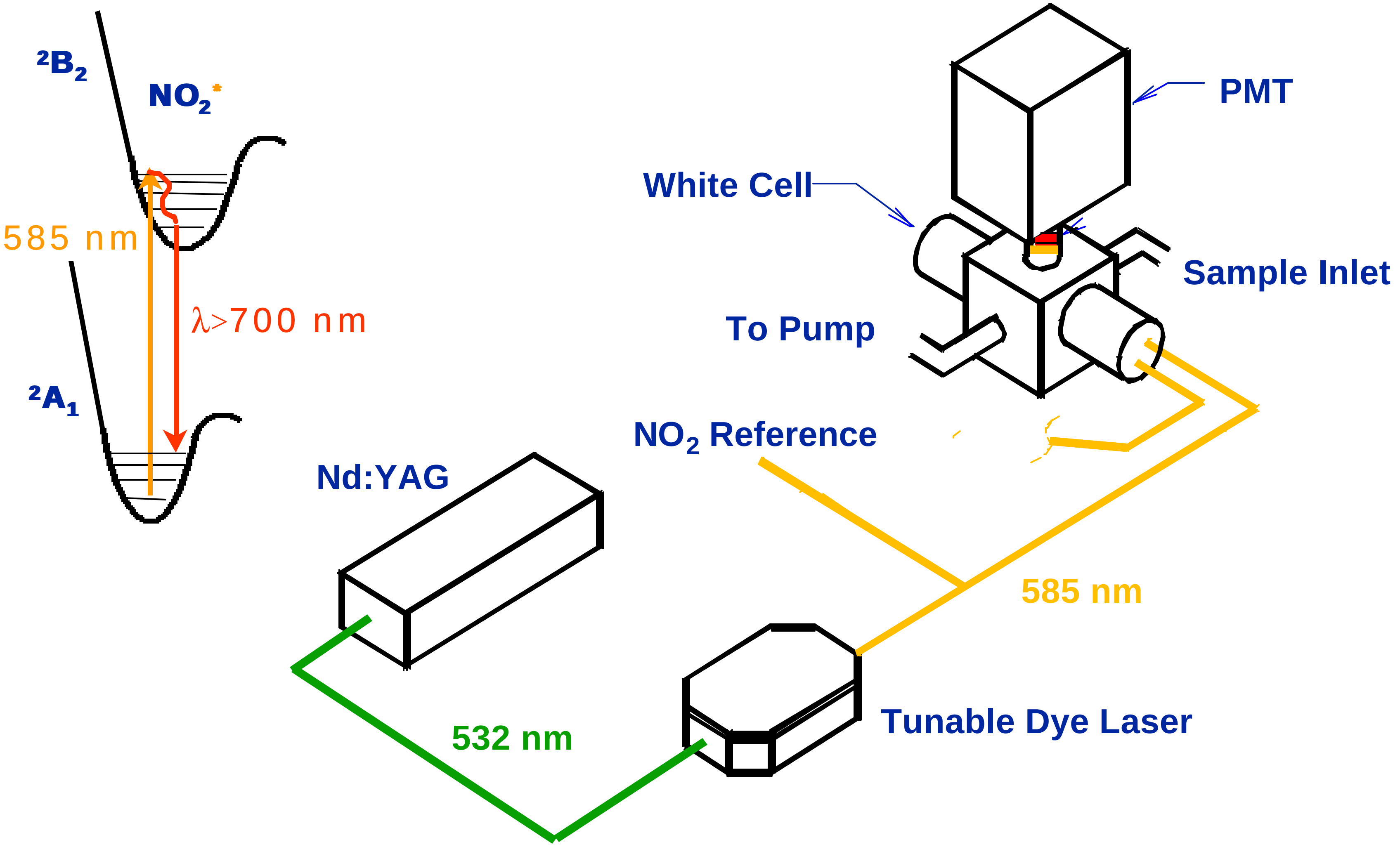
Anal. Chem. **72**, 528 2000

- **Direct and specific**
- **accurate: ±5%, 1s**
- **sensitive: 6ppt/min, S/N=2**
- **detection limit 1ppt**

Since 2000

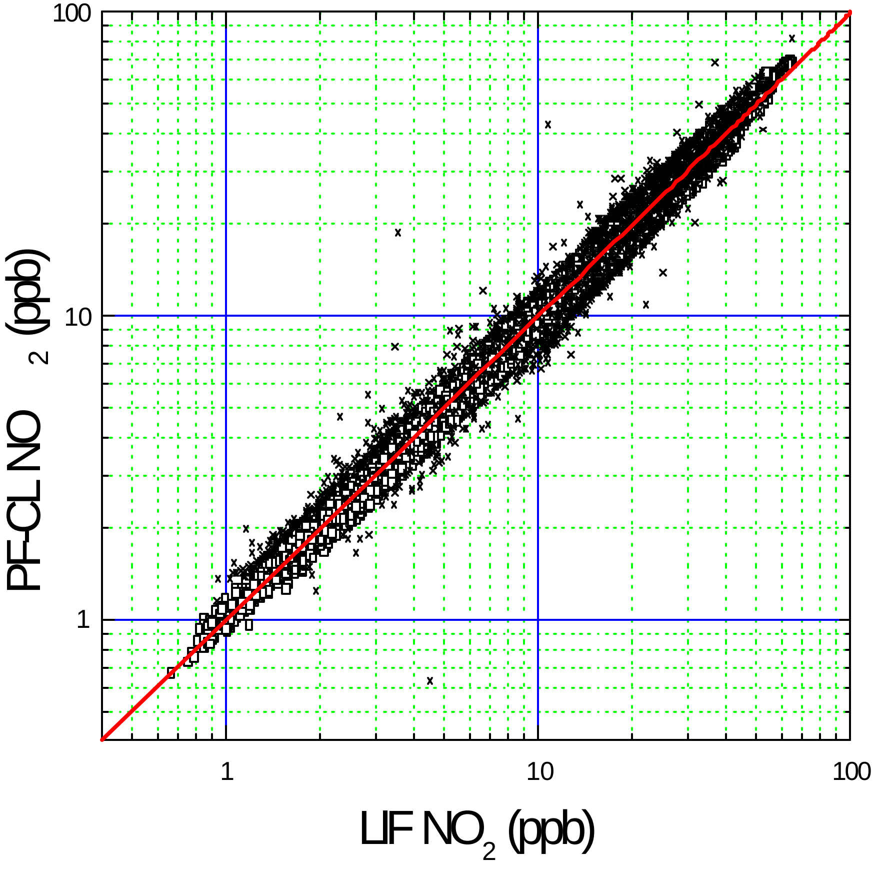
- **sensitivity <1ppt/min**
- **~7 days unattended**

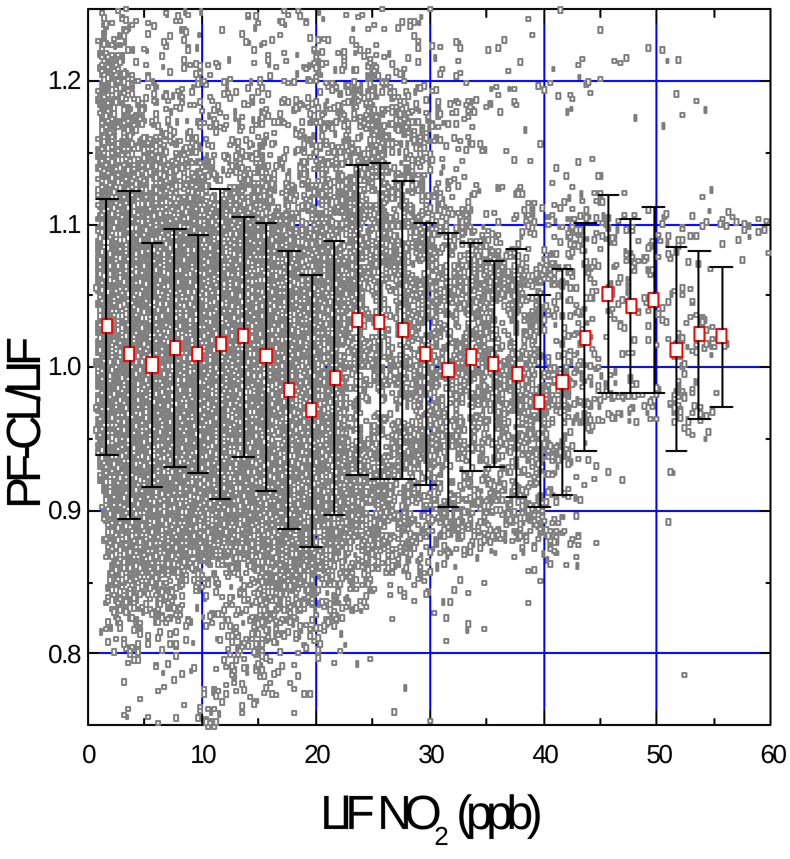
LIF detection of NO_2



Analytical Chemistry, 72, 528, 2000

NO_2 Instrument Comparison (SOS 99)





Diode laser (Patti Cleary)

Applied Optics **41**(33), 6950, 2002

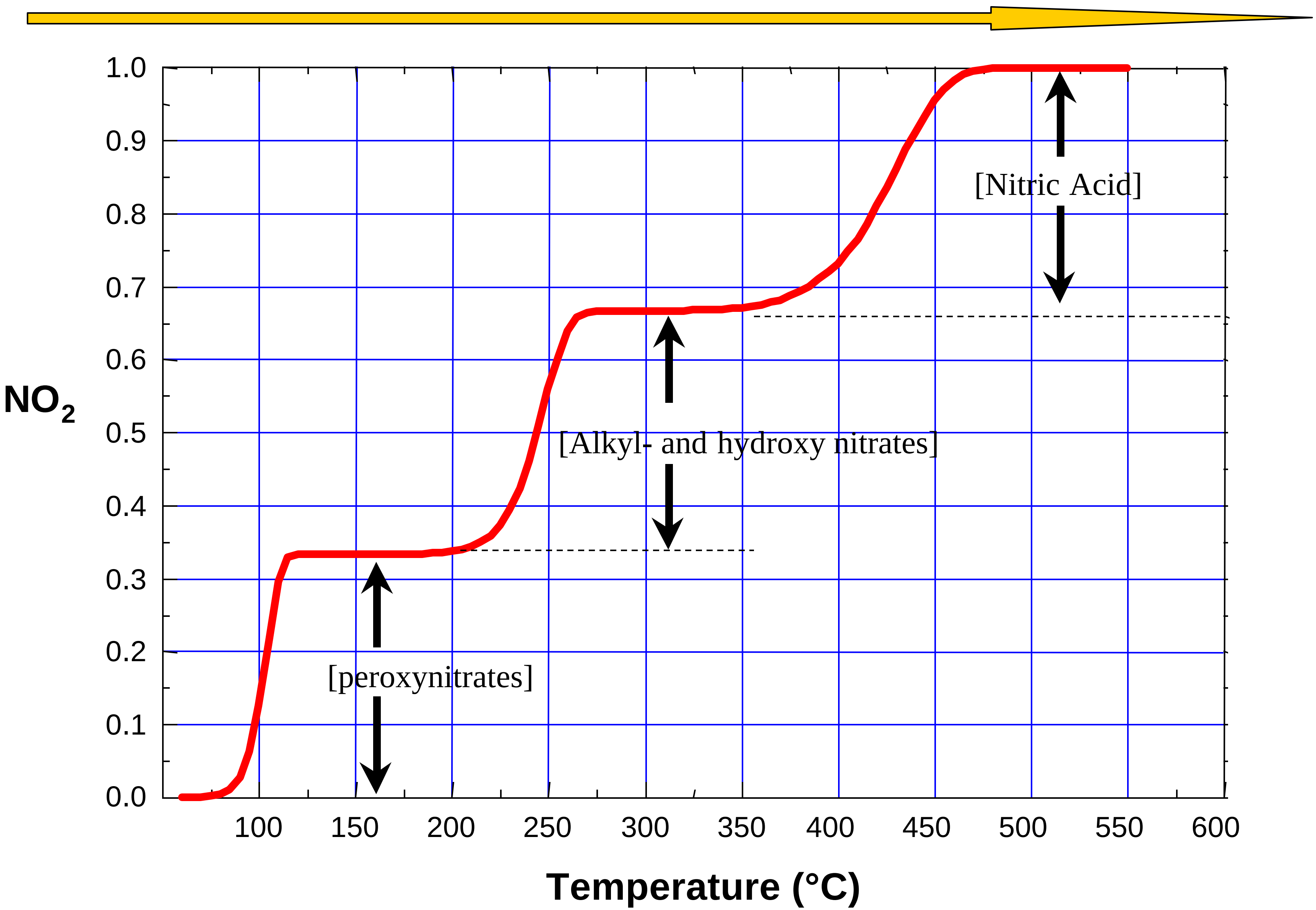
- **638nm laser and a ss-jet**
- **sensitivity of 75ppt/min**
- **130lbs**
- **weeks without an operator**

ΣPNs, ΣANs, & HNO_3 + heat $\rightarrow$ $RO_x + NO_2$

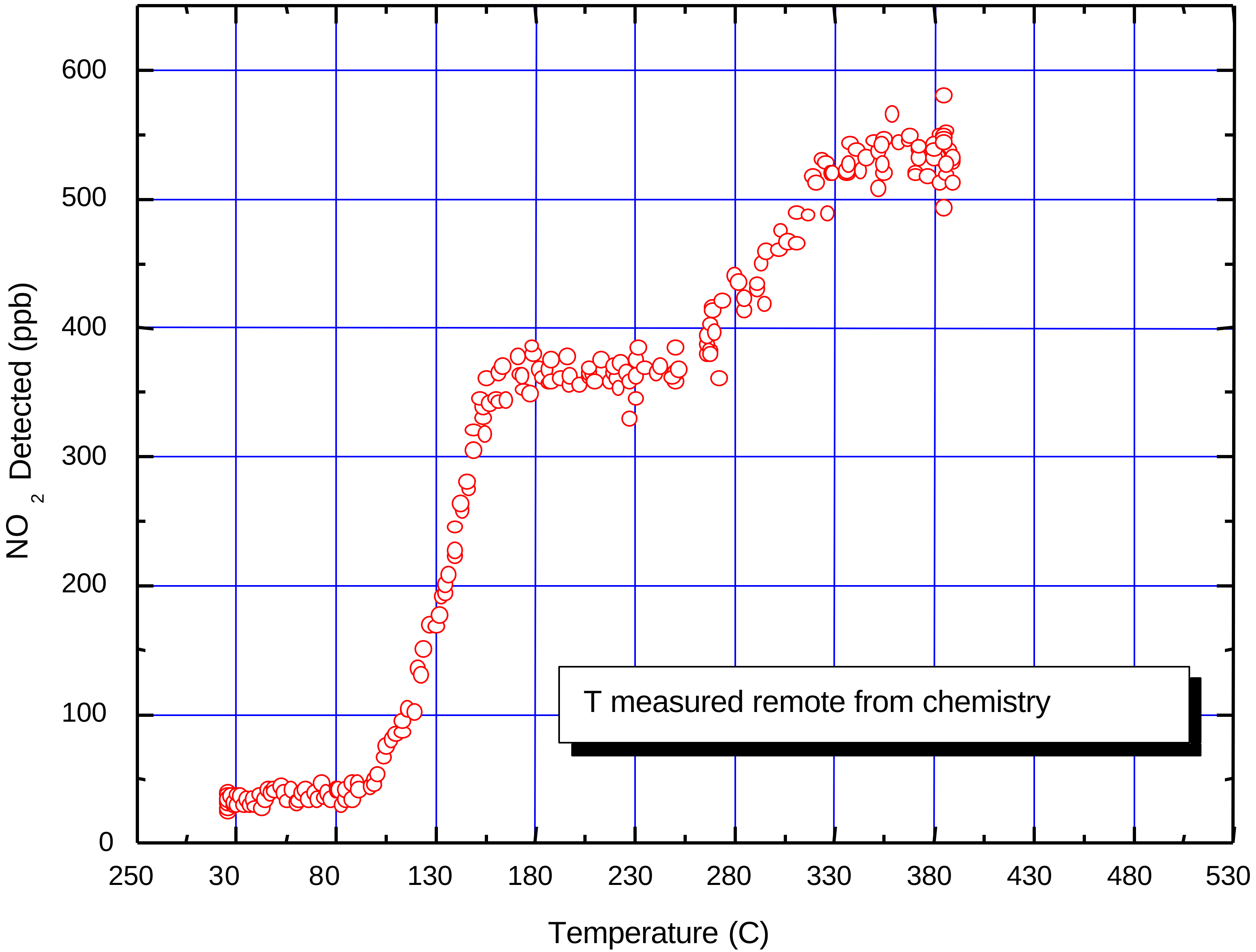
Thermal Dissociation-LIF

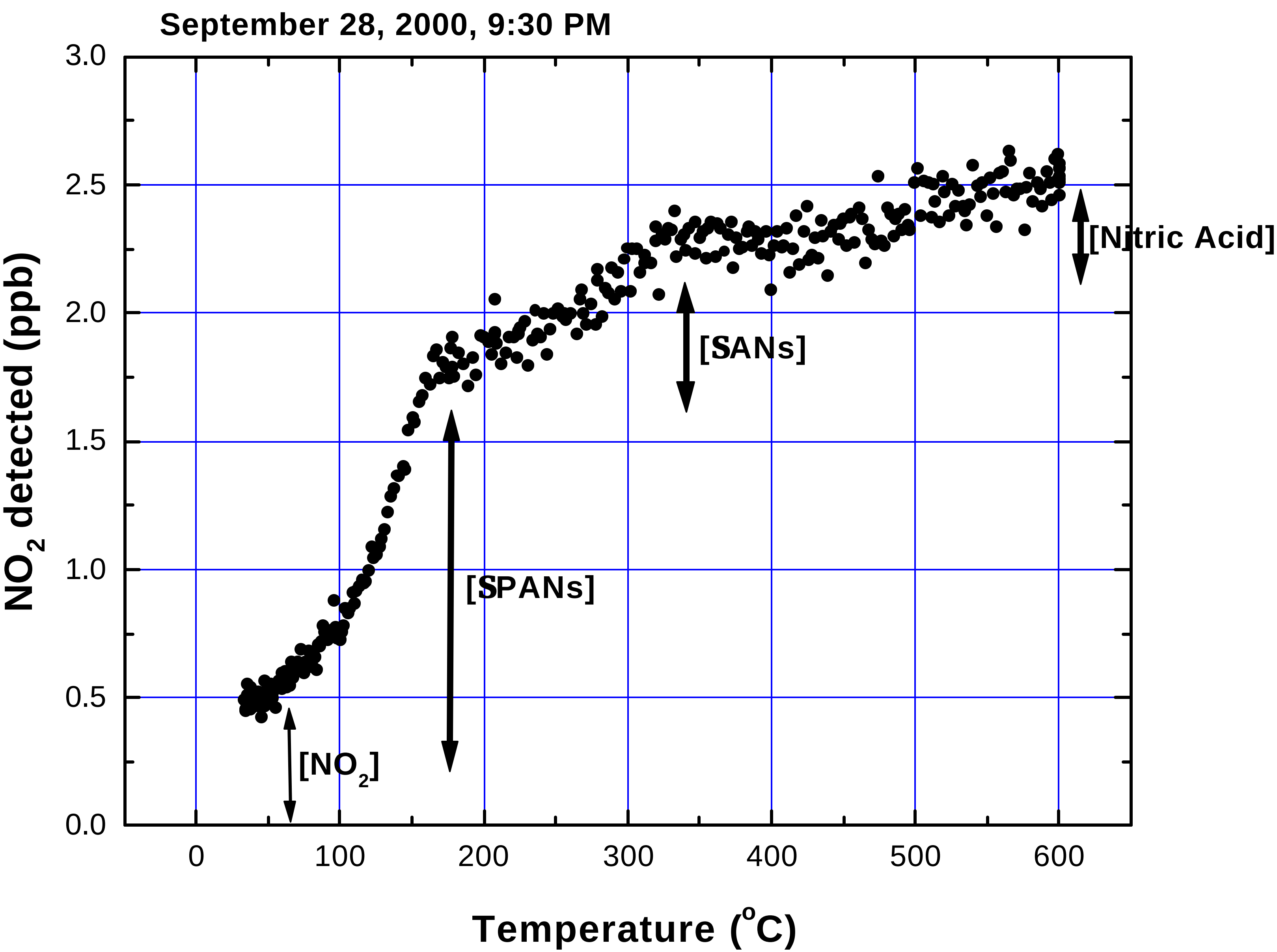
Doug A. Day, et al, JGR., **107(D6)**, ‘02.

ΣPNs, ΣANs, & HNO_3 + heat $\rightarrow$ RO_x + NO_2



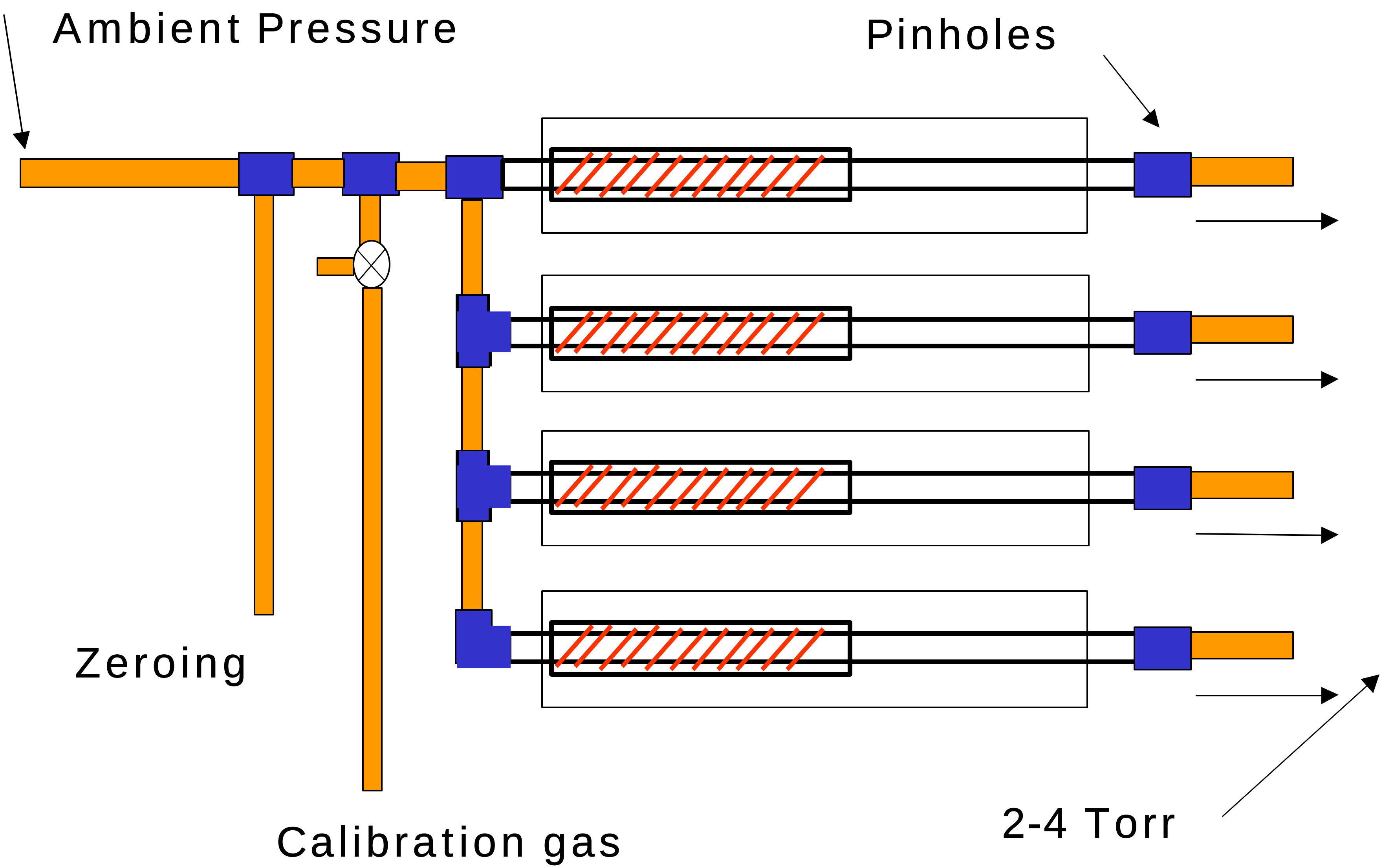
$HONO_2$ and $C_2H_5ONO_2$

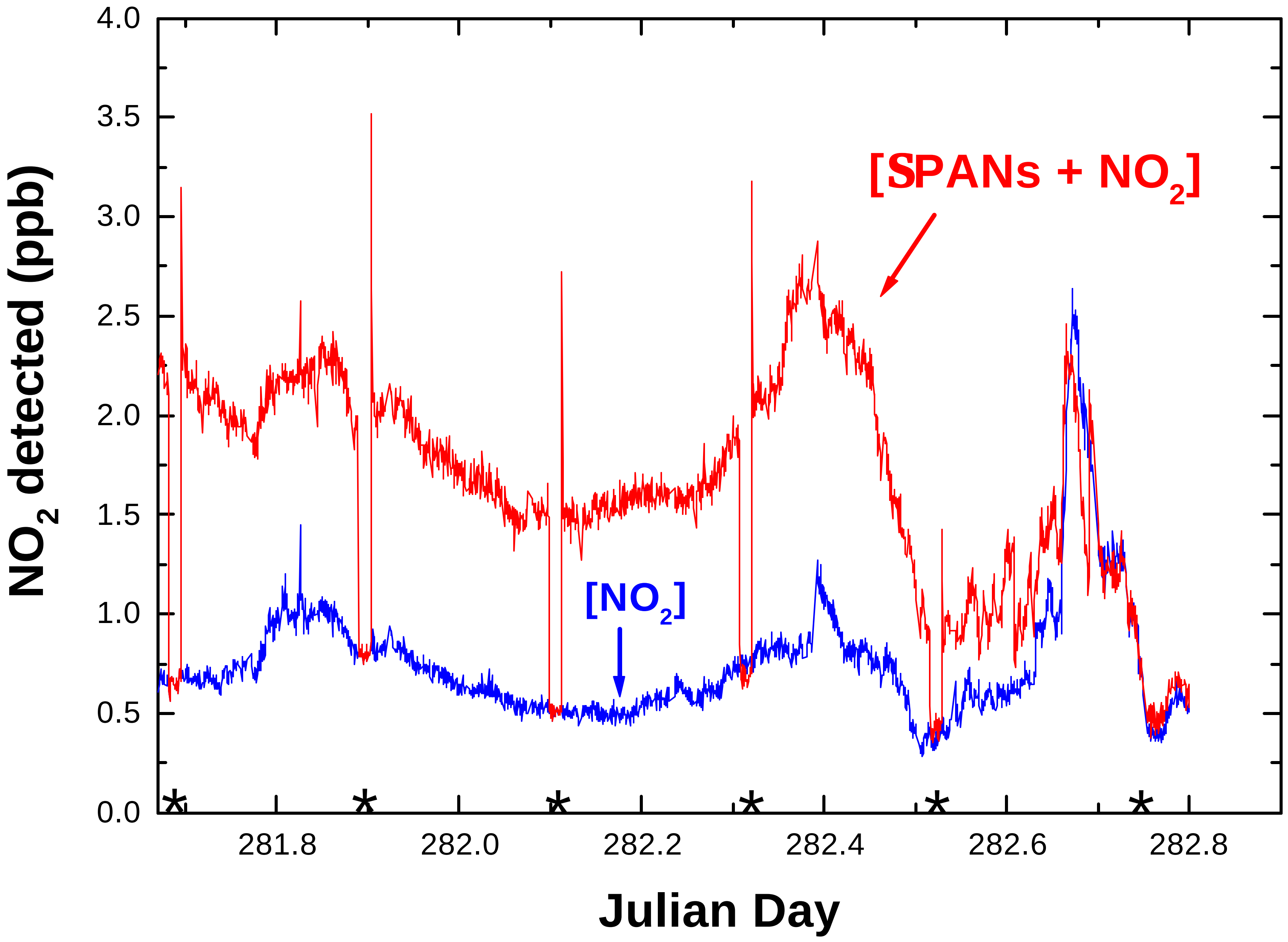




September 28, 2000, 9:30 PM
NO2 detected (ppb)
Temperature (oC)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
[Nitric Acid]
[SANs]
[SPANs]
[NO2]

Inlet and Dissociation Heaters





[SPANs + NO2]
[NO2]
NO2 detected (ppb)
Julian Day
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
281.8
282.0
282.2
282.4
282.6
282.8

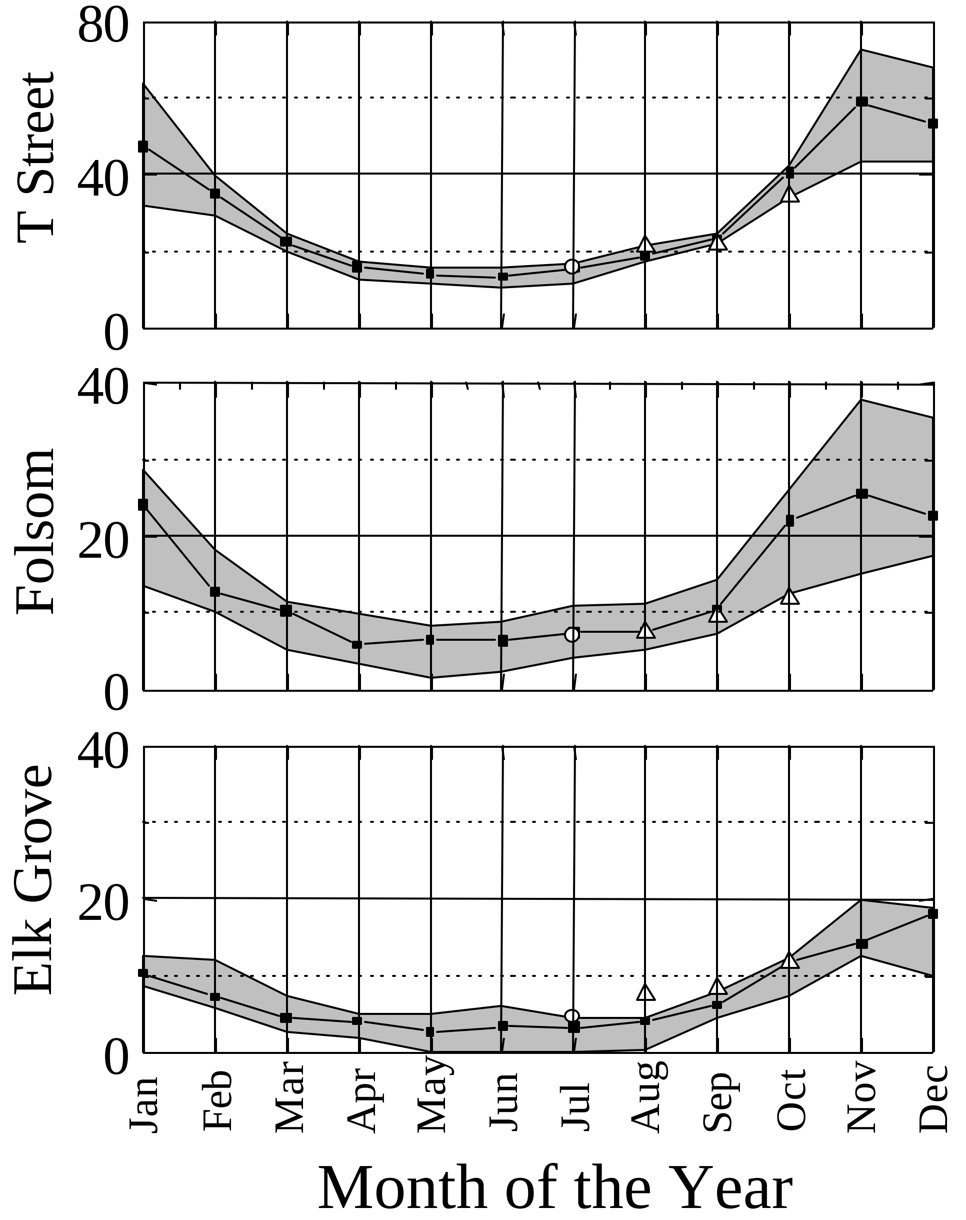
TD-LIF

Accuracy 15%

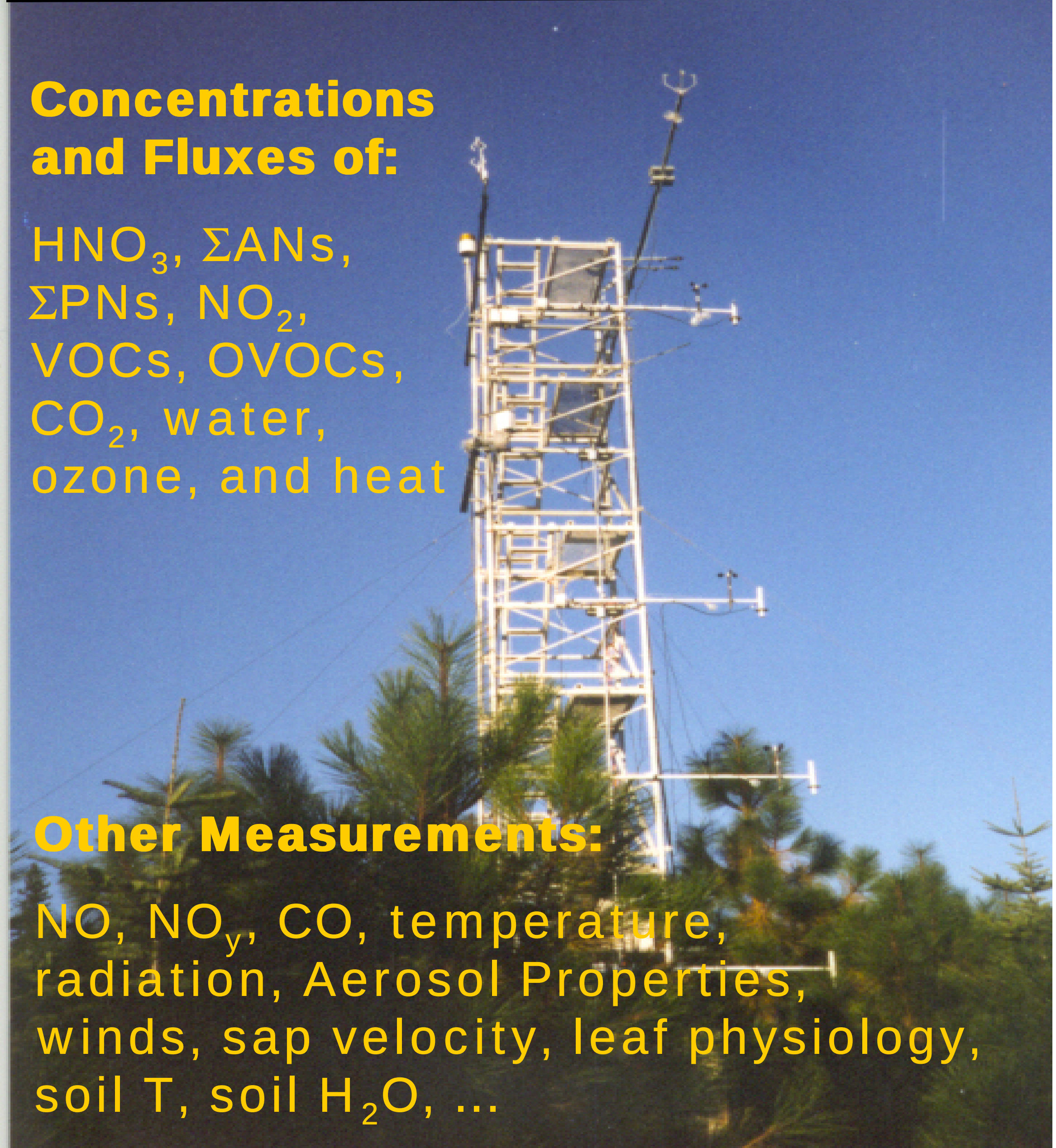
Sensitivity ~10 ppt

Used at
UC-Blodgett Forest, CA
Granite Bay, CA
Big Hill, CA
Houston, TX and
from the NCAR C-130 (0-7km ASL 35°-85°N Latitude)

Daytime NO_x (ppb) in the Sacramento Area



Blodgett Forest 12 m Tower

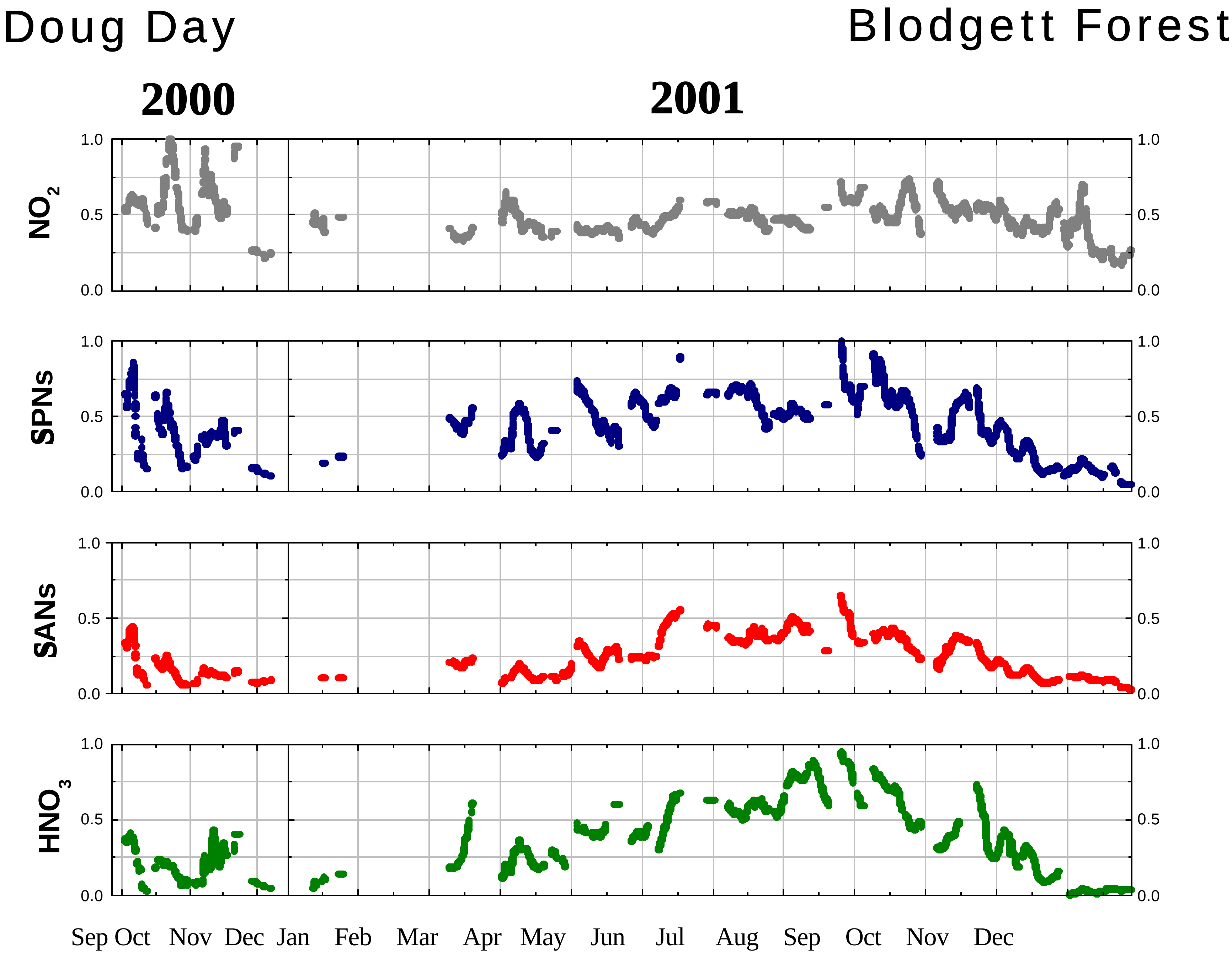


Concentrations and Fluxes of:

HNO_3, ΣANs, ΣPNs, NO_2, VOCs, OVOCs, CO_2, water, ozone, and heat

Other Measurements:

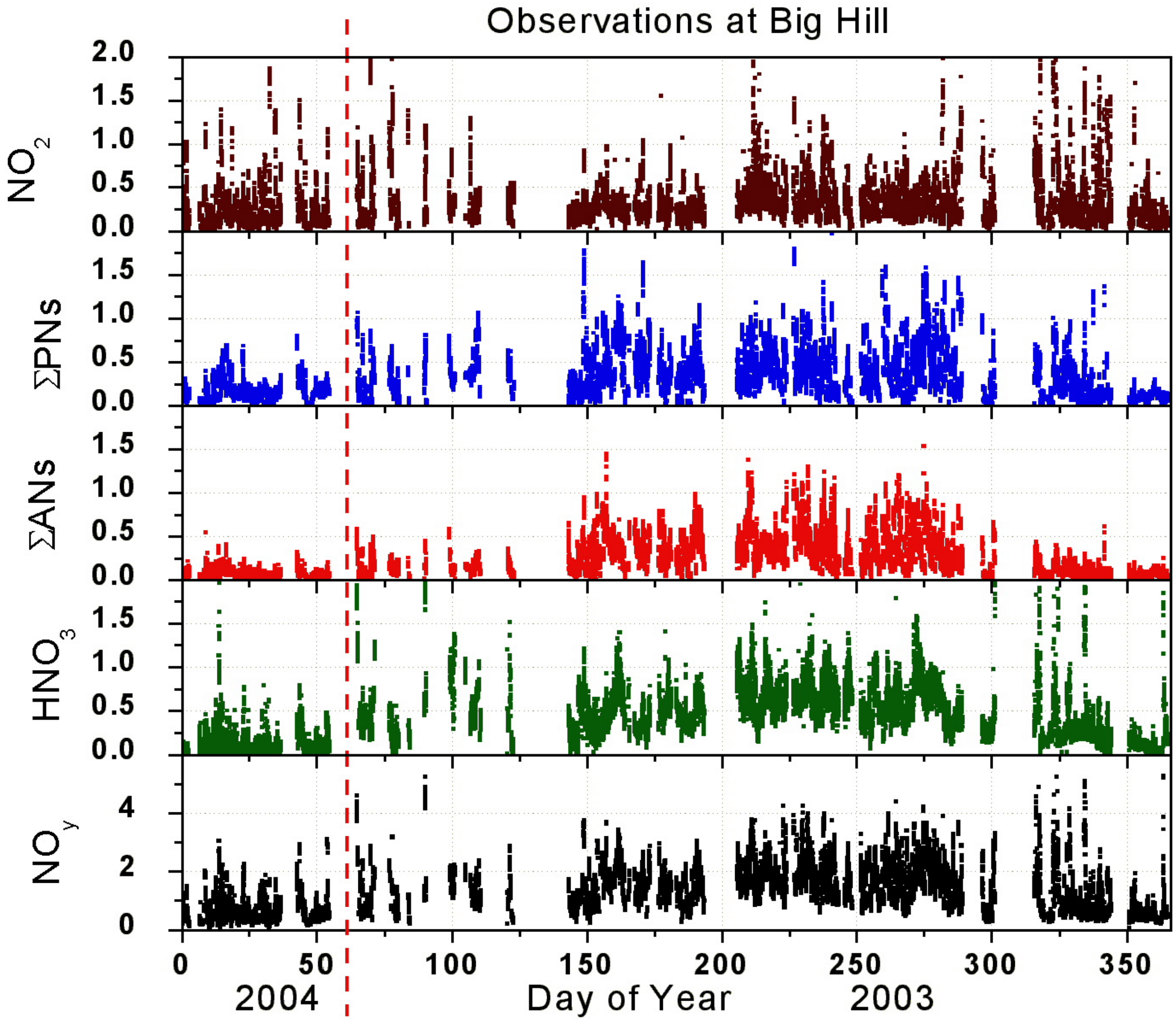
NO, NO_y, CO, temperature, radiation, Aerosol Properties, winds, sap velocity, leaf physiology, soil T, soil H_2O, ...



Doug Day
Blodgett Forest
2000
2001
NO2
SPNs
SANs
HNO3
1.0
0.5
0.0
Sep Oct Nov Dec Jan Feb Mar Apr May Jun Jul Aug Sep Oct Nov Dec

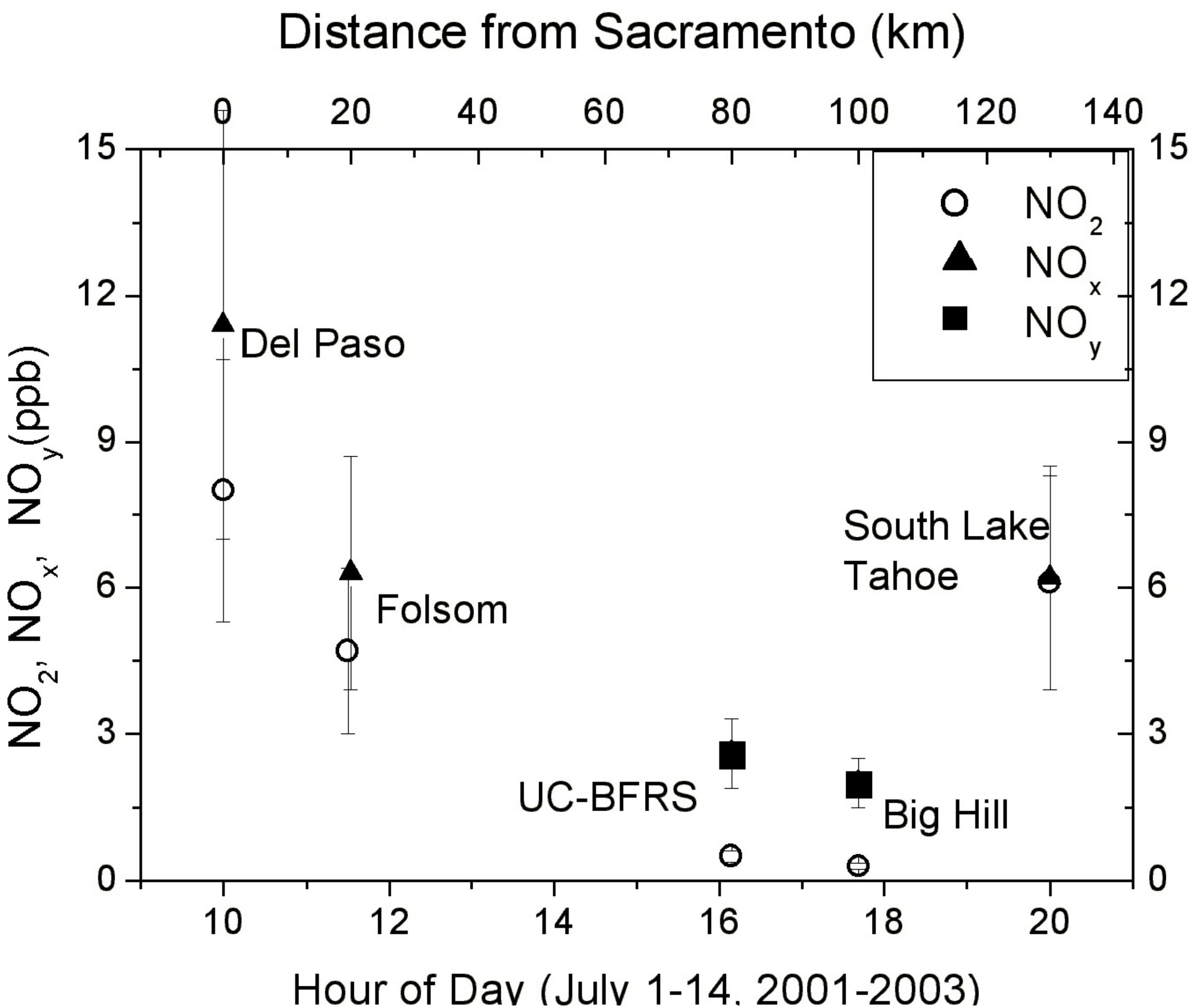
Big Hill Observations from Tower atop trailer

Jennifer Murphy and Paul Wooldridge

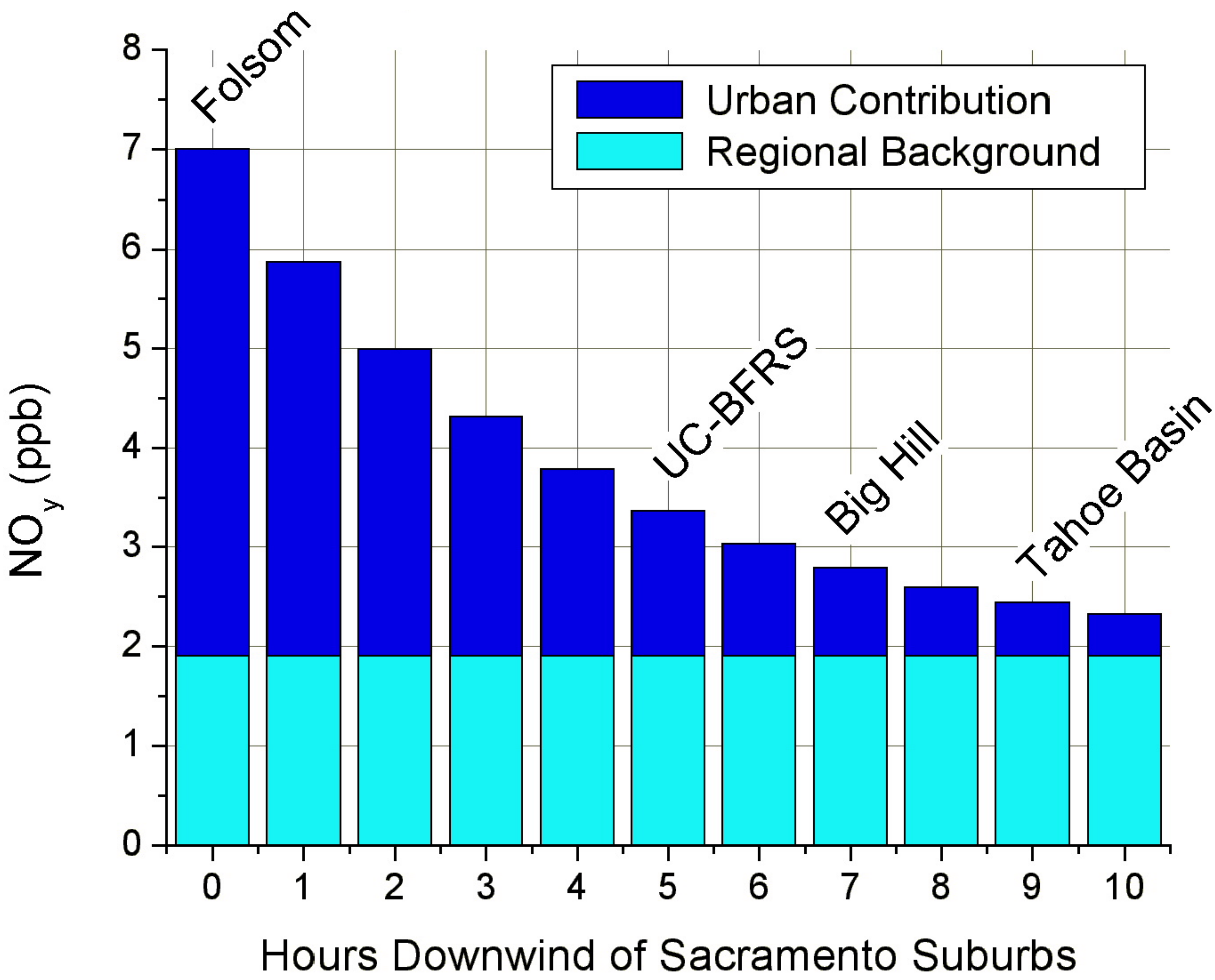


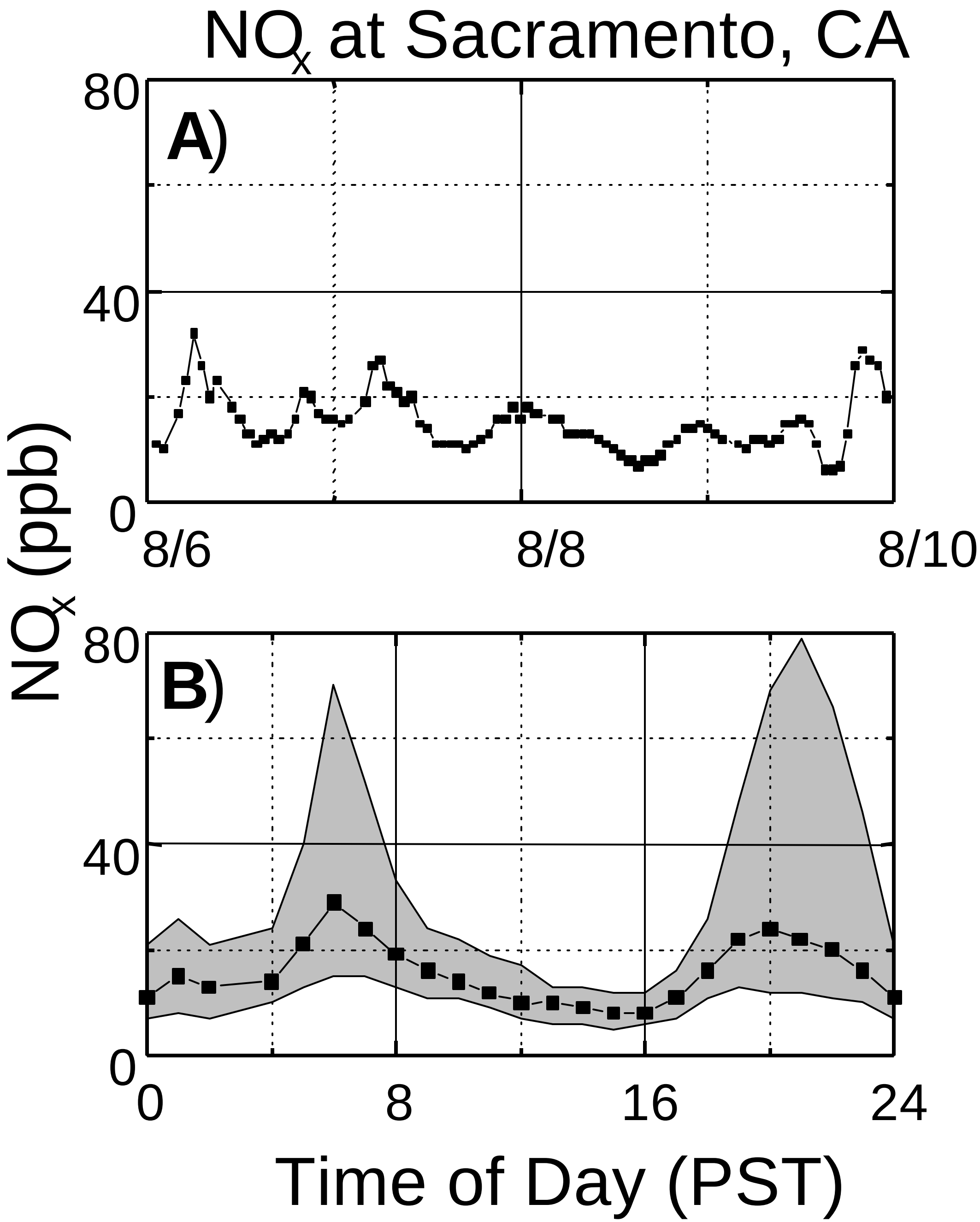
Preliminary

Summertime plume



Pure transport contribution to NO_y (an upper limit)

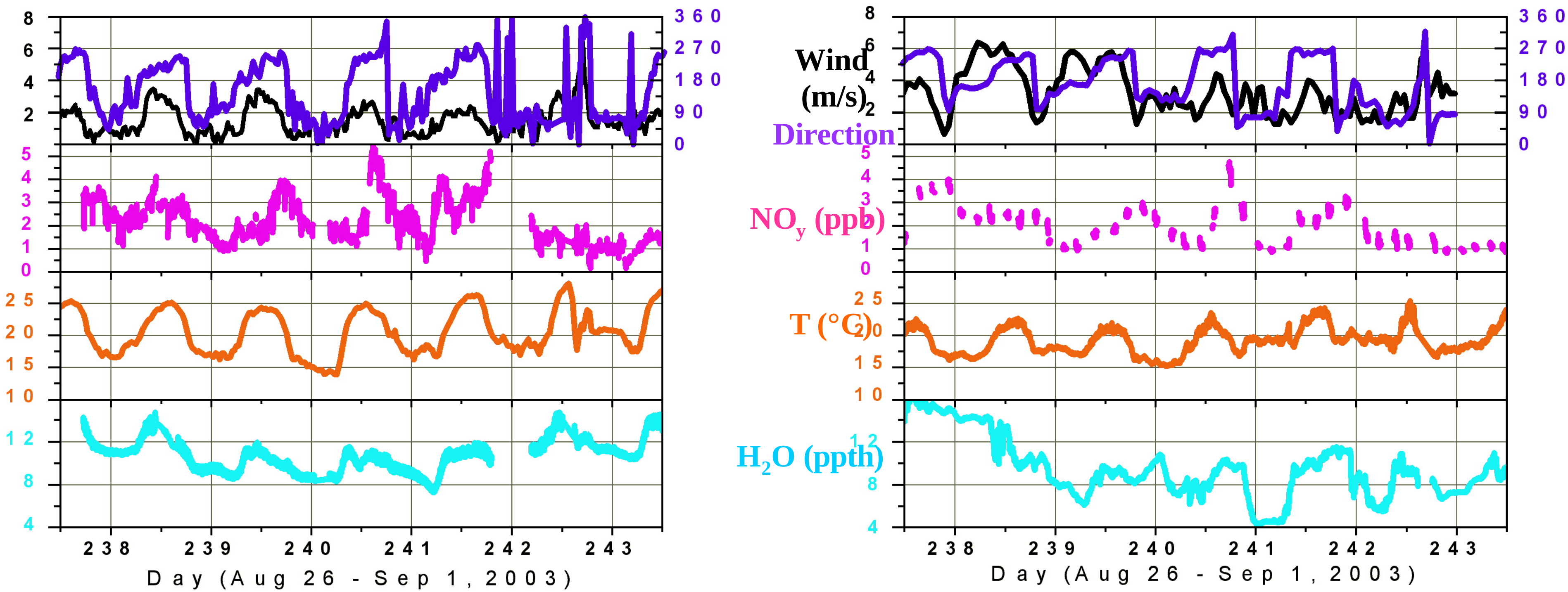




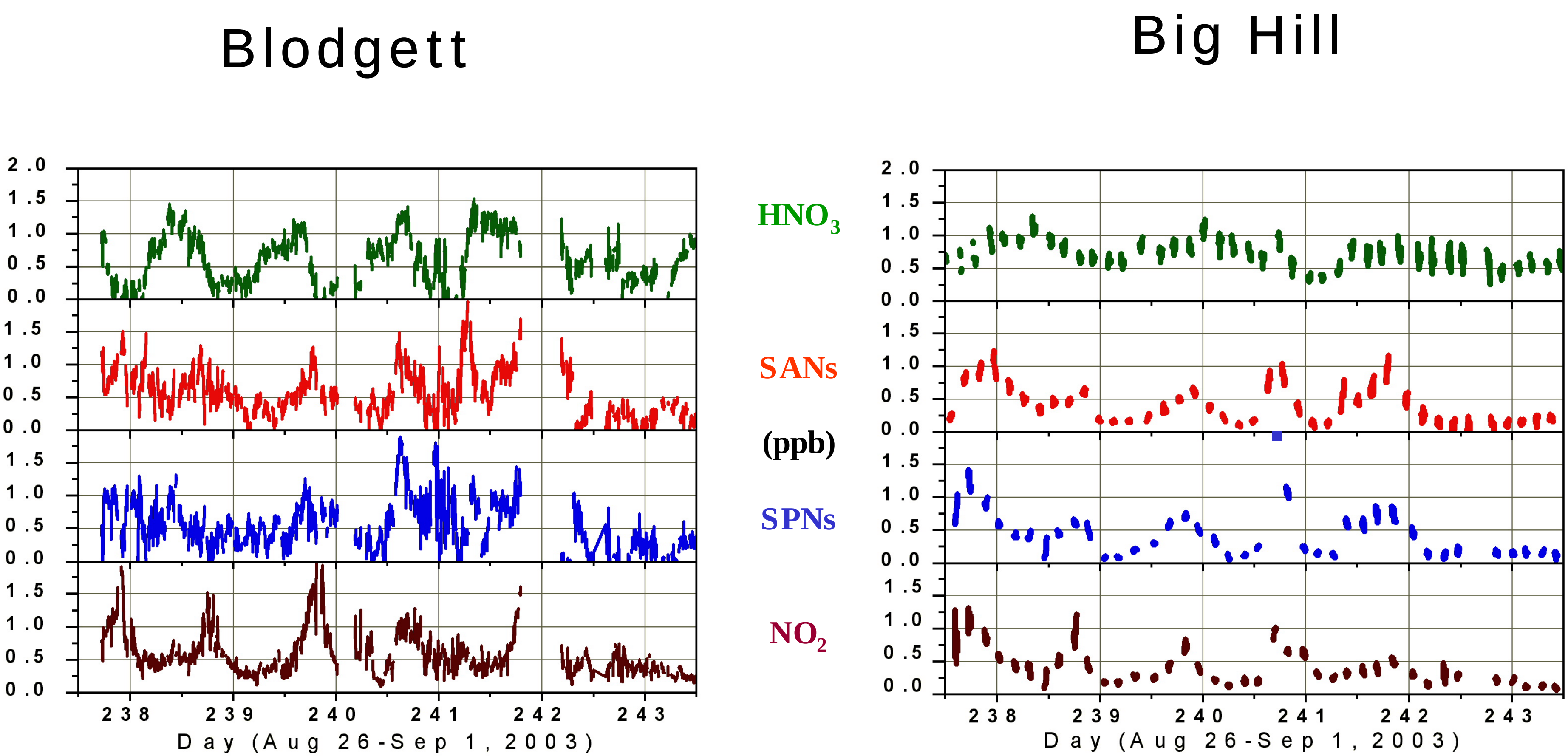
NOx at Sacramento, CA
A)
80
40
0
8/6
8/8
8/10
NOx (ppb)
B)
80
40
0
0
8
16
24
Time of Day (PST)

Blodgett

Big Hill

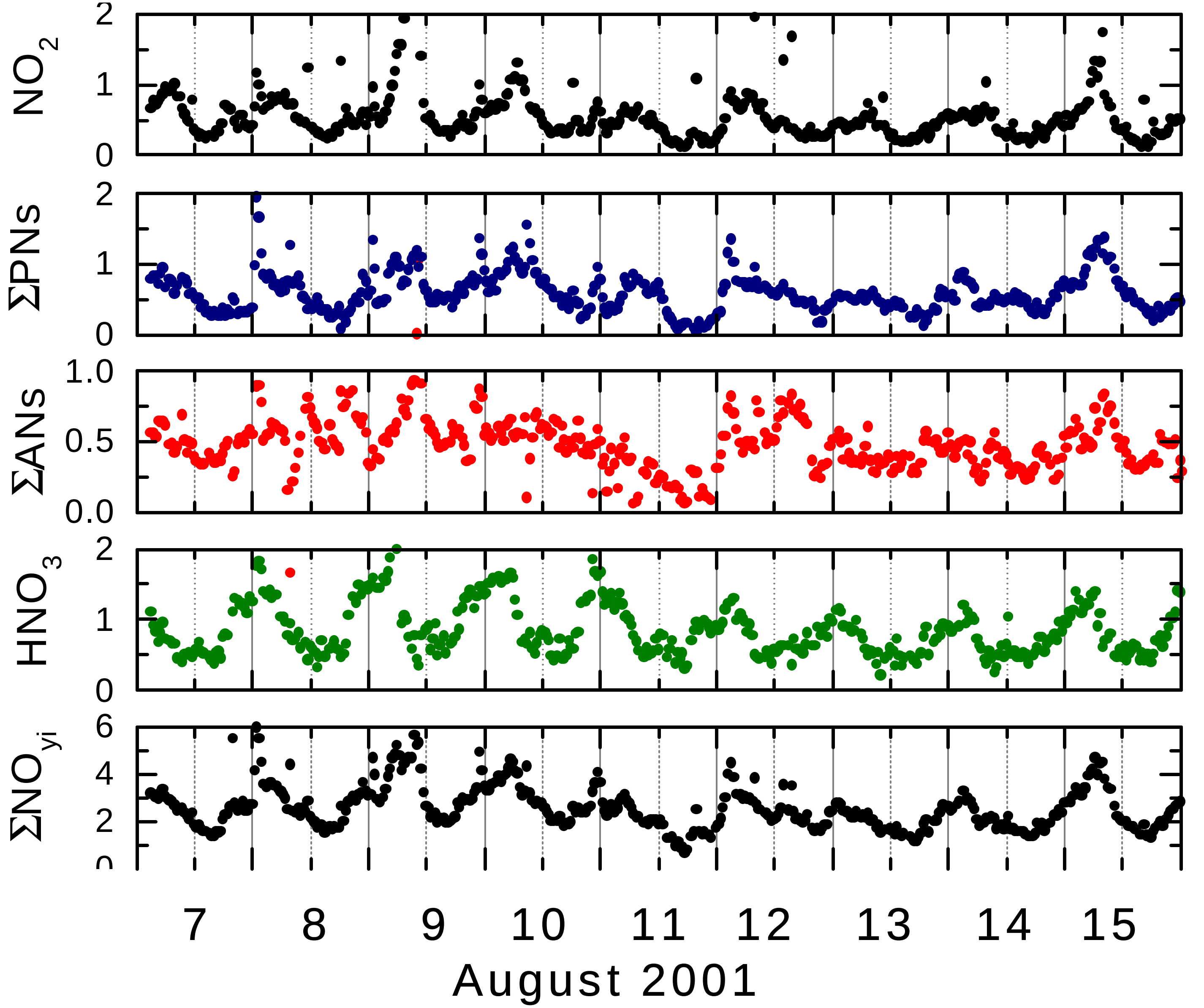


Blodgett has bigger T swings, smaller H_2O swings, slower winds.

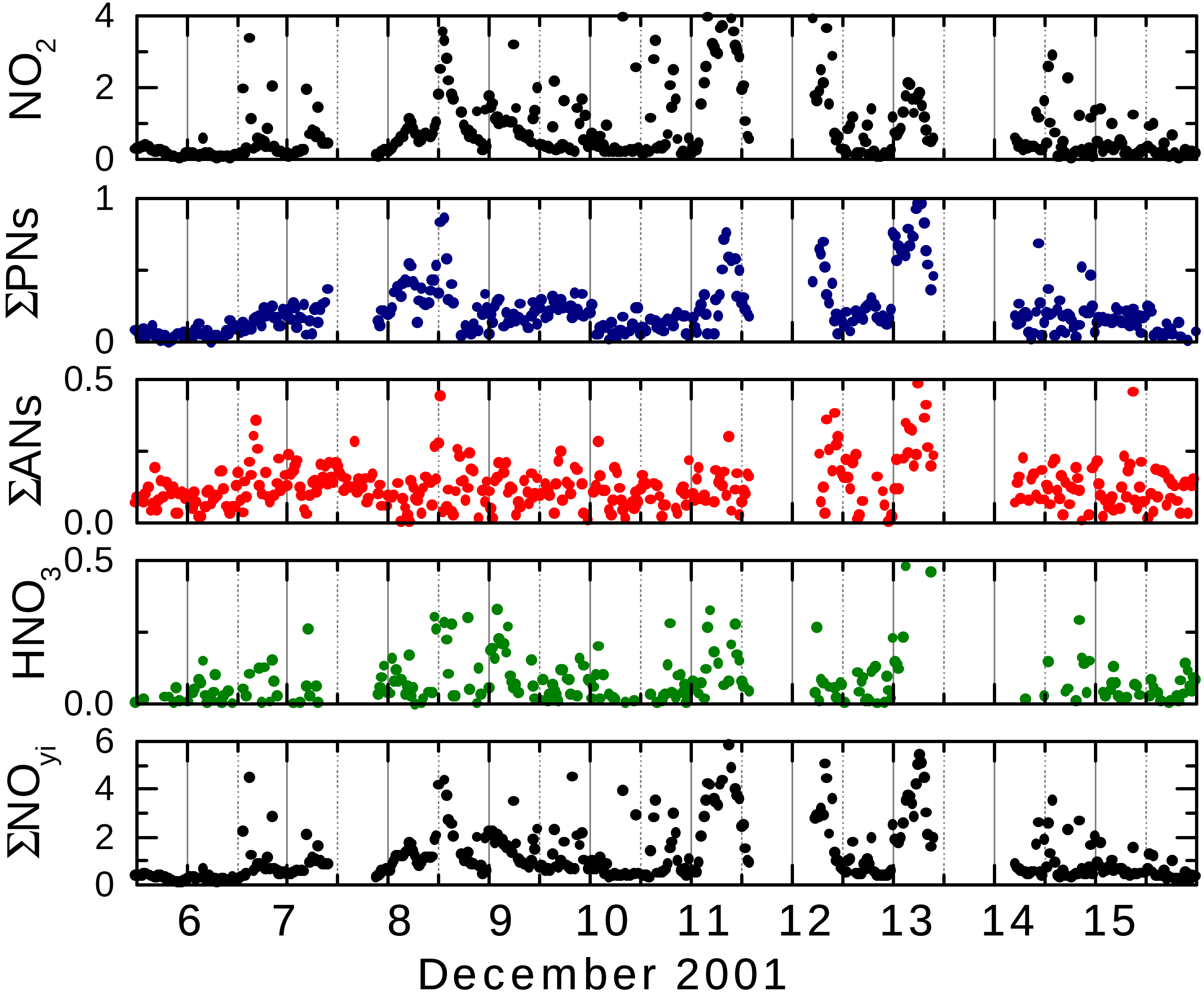


More NO_2 at Blodgett suggests less processed, younger air.
HNO_3 at Big Hill doesn't disappear at night.

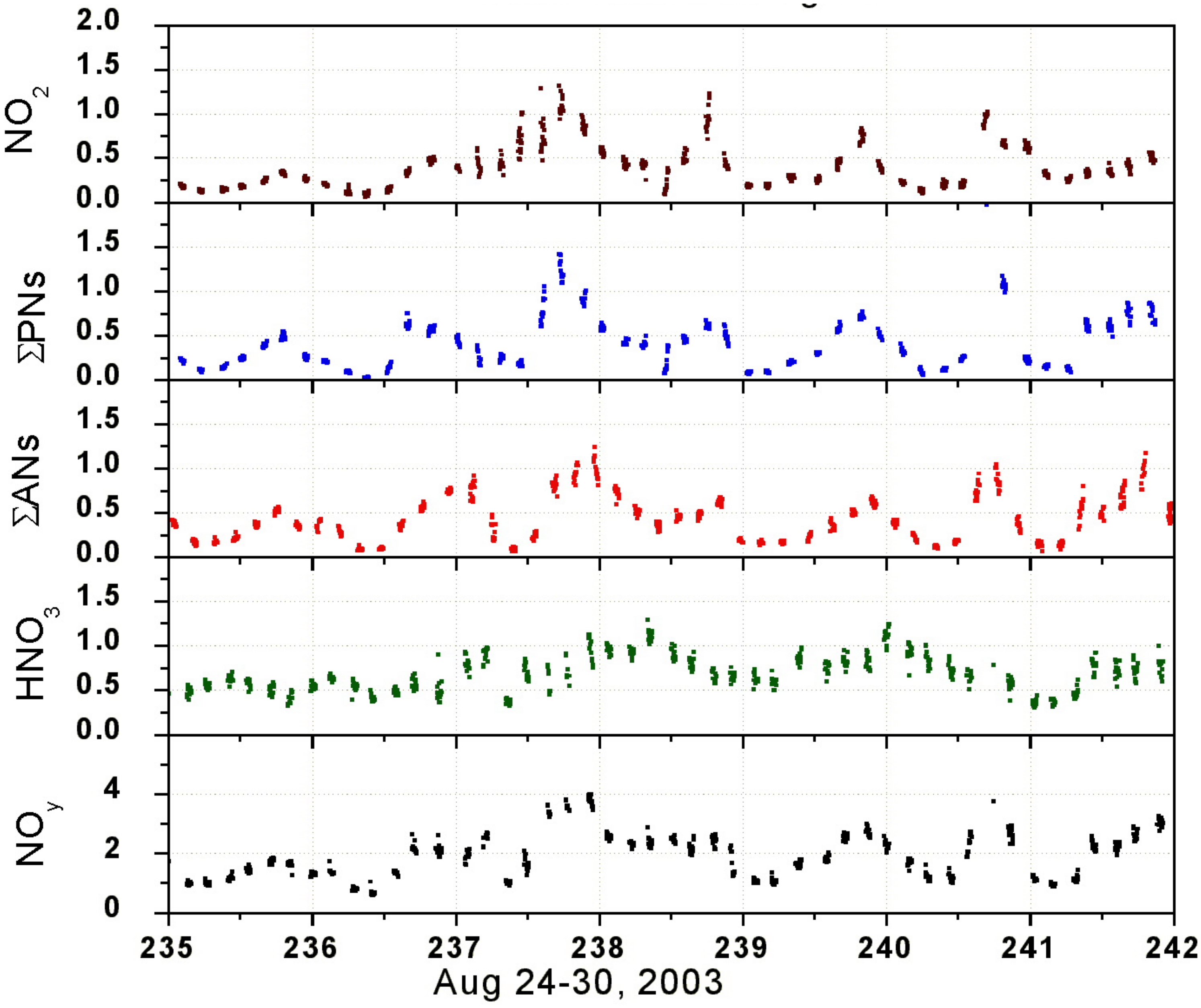
NO_{yi} at UC Blodgett Forest



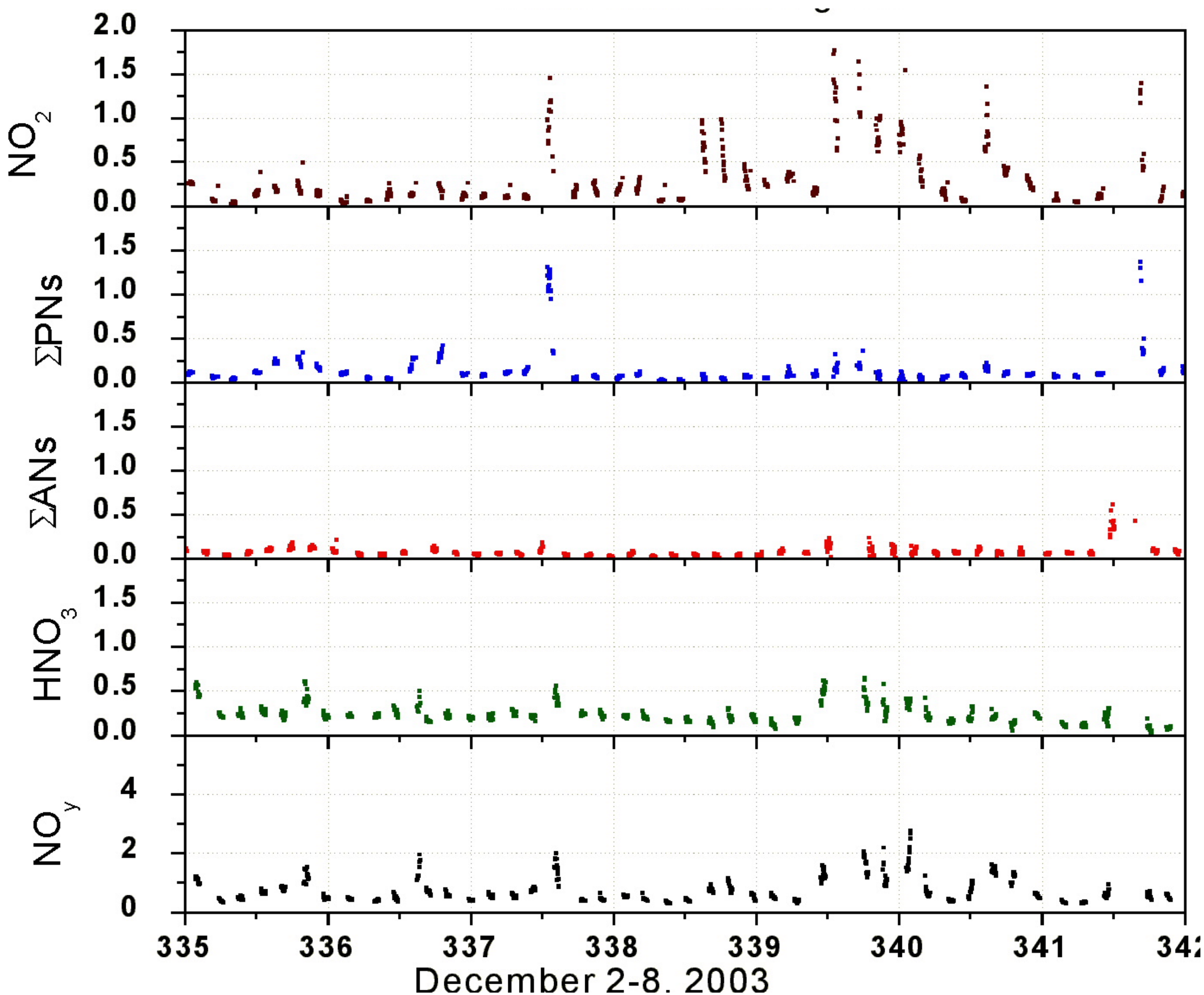
NO_{yi} at UC Blodgett Forest



NO_{yi} at Big Hill

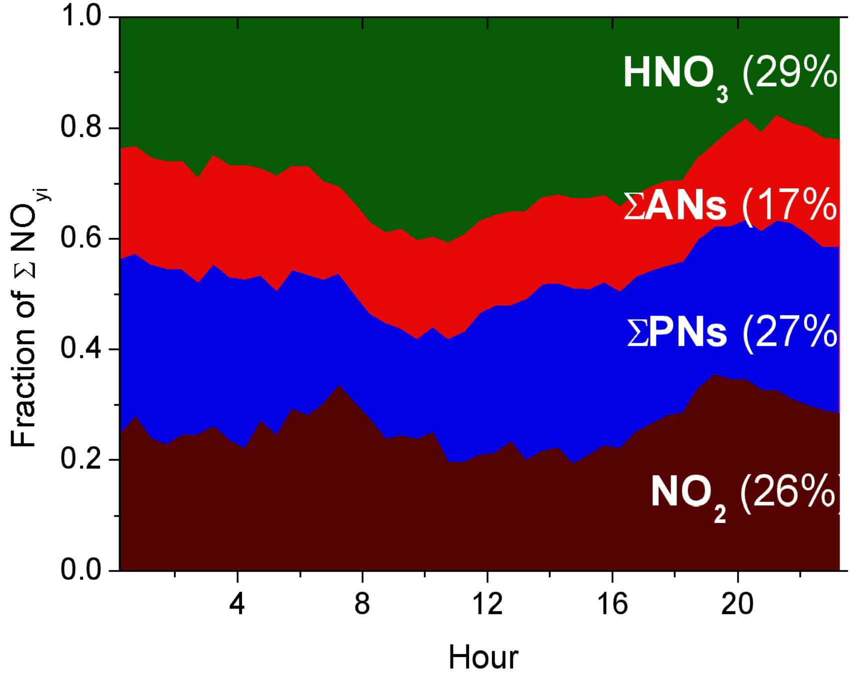


NO_{yi} at Big Hill

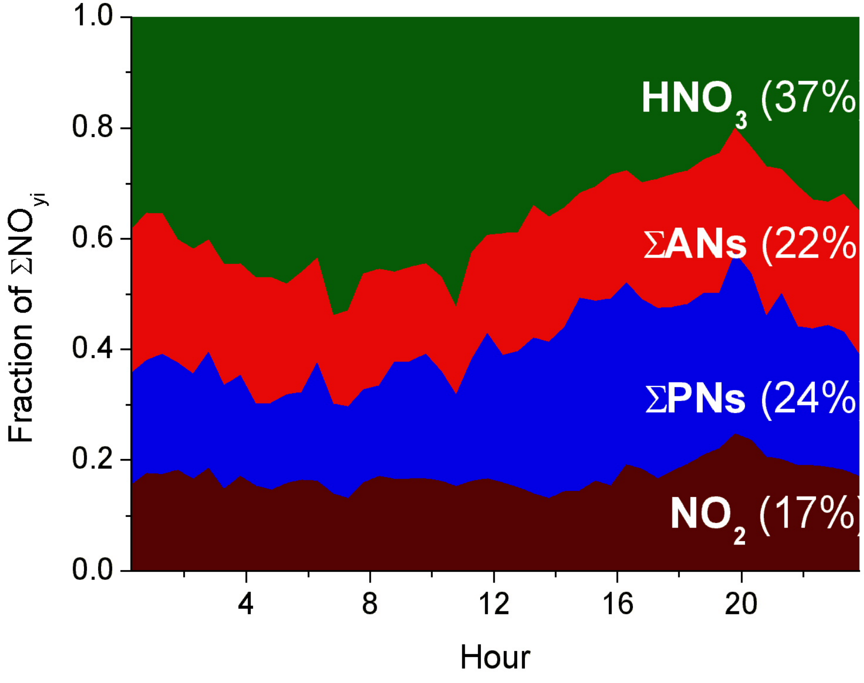


Summer

Blodgett Forest 2001

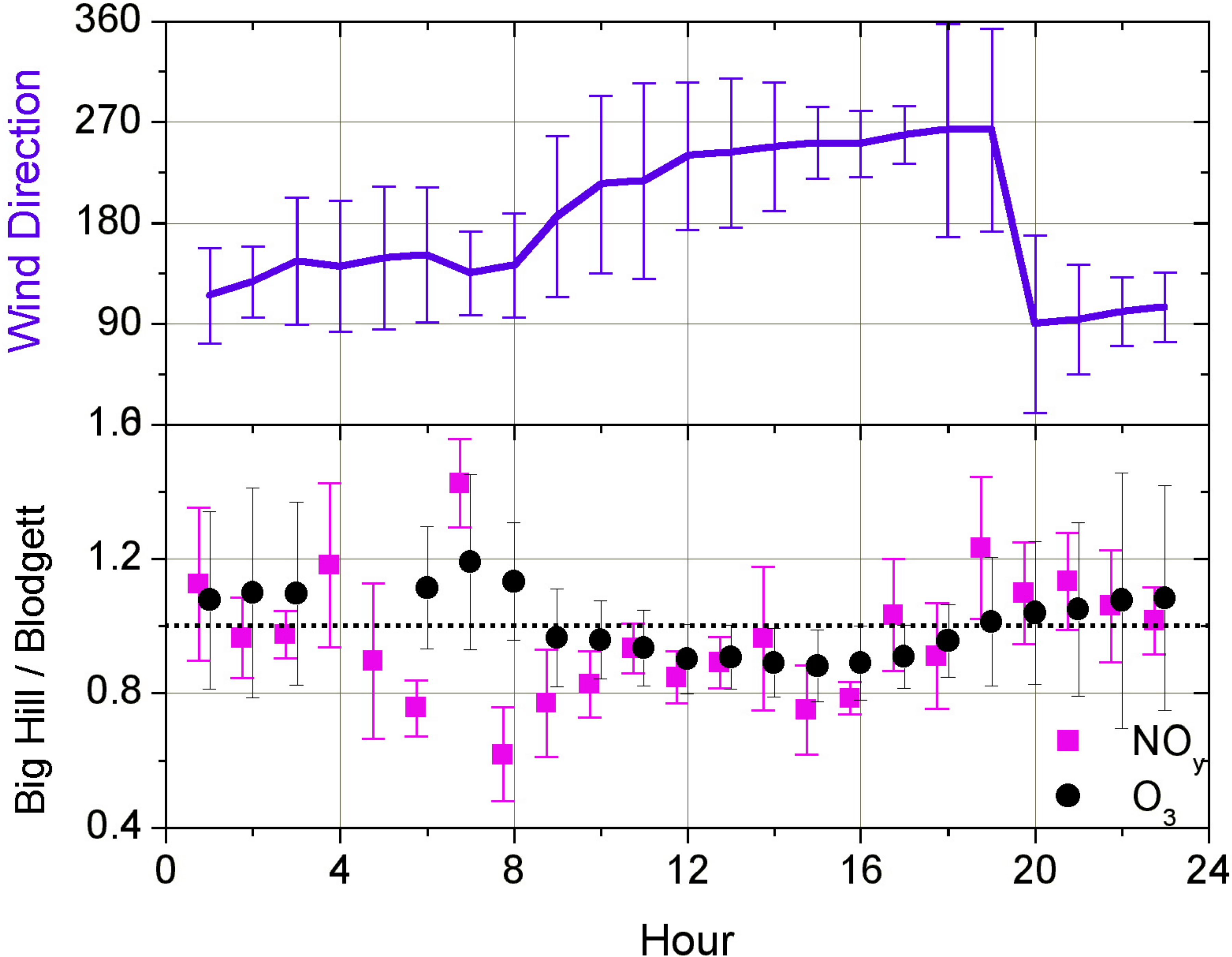


Big Hill 2003



The two sites sample similar air during the day.

Reactive nitrogen at Big Hill is more oxidized and diluted.



Wind Direction
360
270
180
90
1.6
1.2
0.8
0.4
Big Hill / Blodgett
NO$_y$
O$_3$
0
4
8
12
16
20
24
Hour

HNO_3

- Day

k_{OH+NO2} $[OH][NO_2] \cong k_{deposition}[HNO_3]$ or

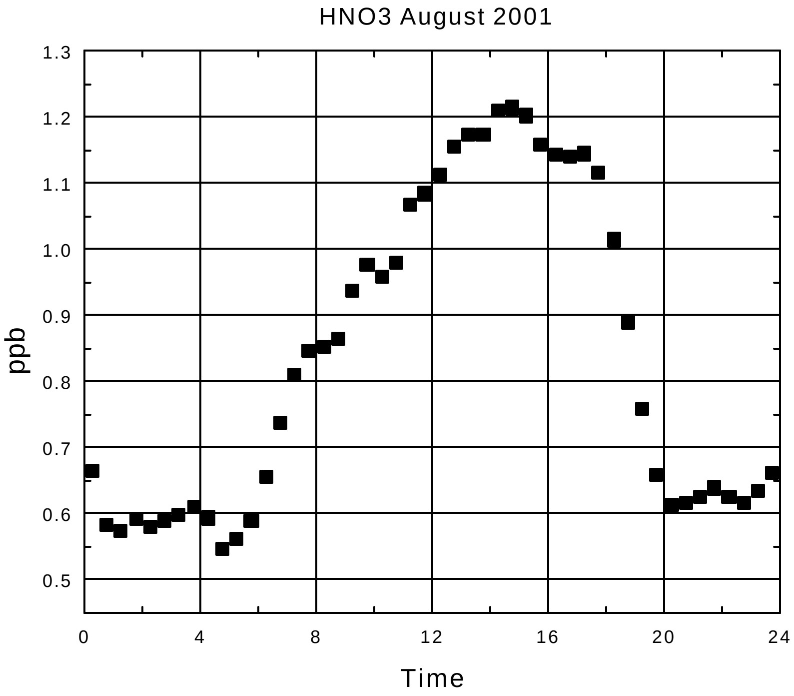
k_{OH+NO2} $[OH]/k_{deposition} \cong [HNO_3]/[NO_2]$

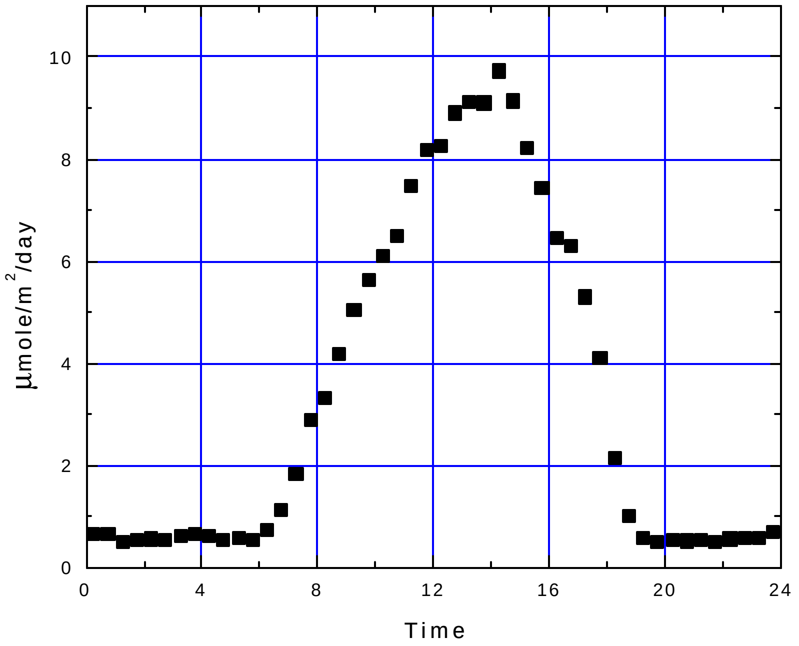
Expect $[HNO_3]/[NO_2]$ to follow OH since k's are roughly constant and fast.

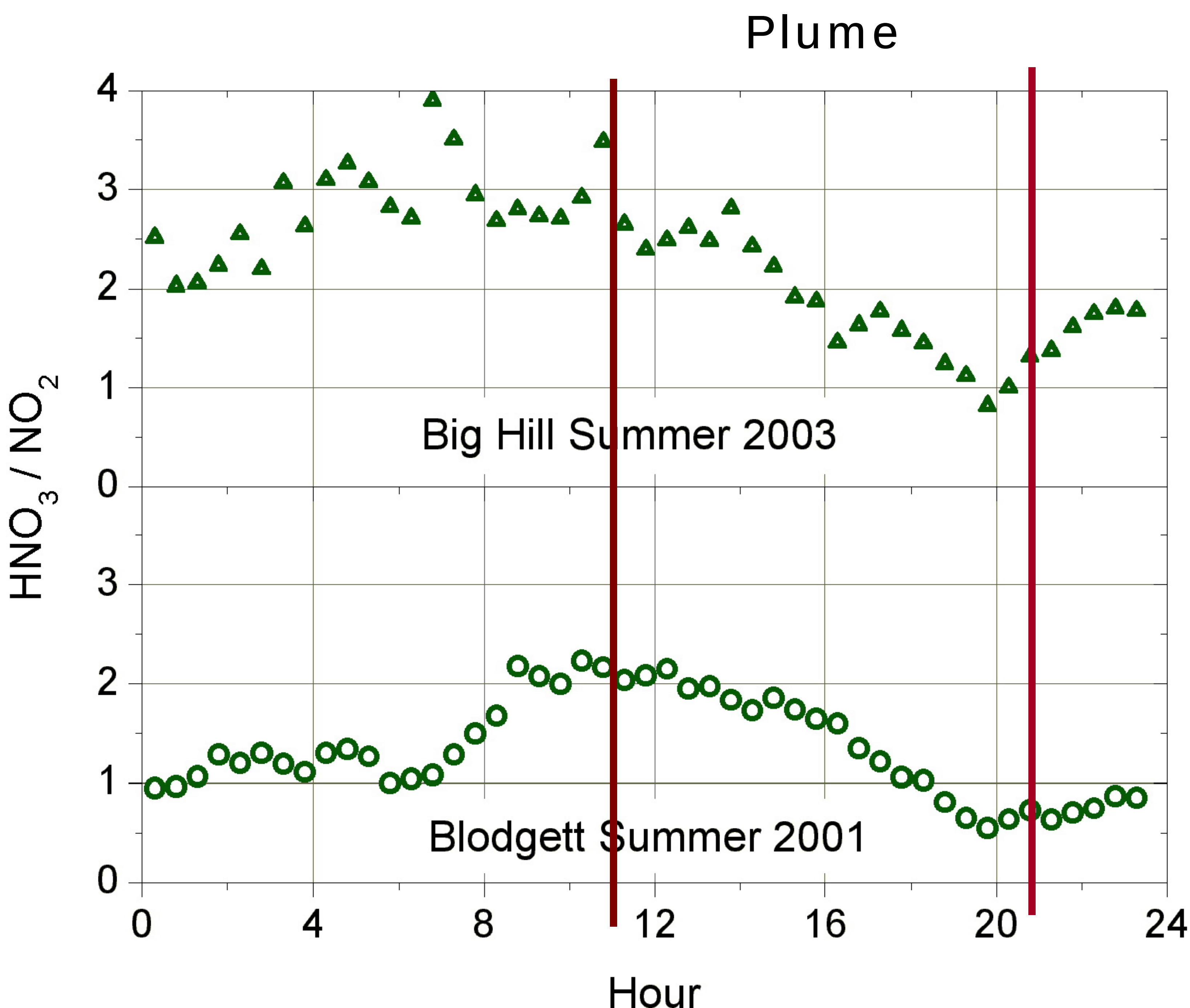
- Night

Chemistry of NO_3 and deposition approaches zero.

Blodgett Forest deposition of HNO_3






Plume
Big Hill Summer 2003
Blodgett Summer 2001
HNO_3 / NO_2
Hour
0
4
8
12
16
20
24
0
1
2
3
4

HNO_3/NO_2 slightly higher at Big Hill than Blodgett, implying deposition is less efficient or OH concentration is higher.

The two sites cannot be perfectly modeled using a single transport path with one effective deposition velocity.

ΣANs and ΣPNs

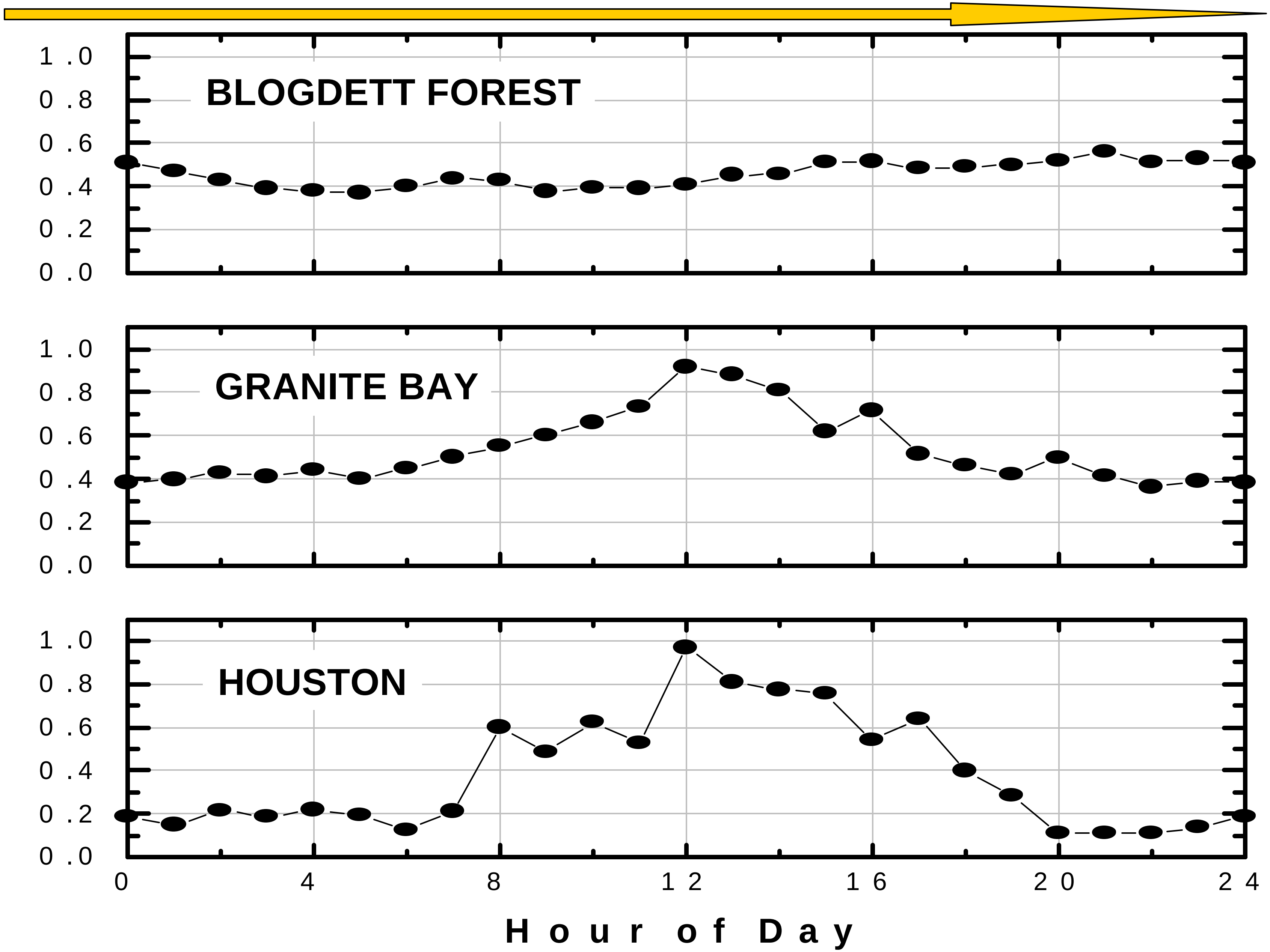
- Day

  Measurements show concentrations follow OH in urban source regions but are decoupled downwind. Implies deposition of ΣANs is rapid (<4 hours) and thermal decomposaition of ΣPNs is rapid (<4 hours).

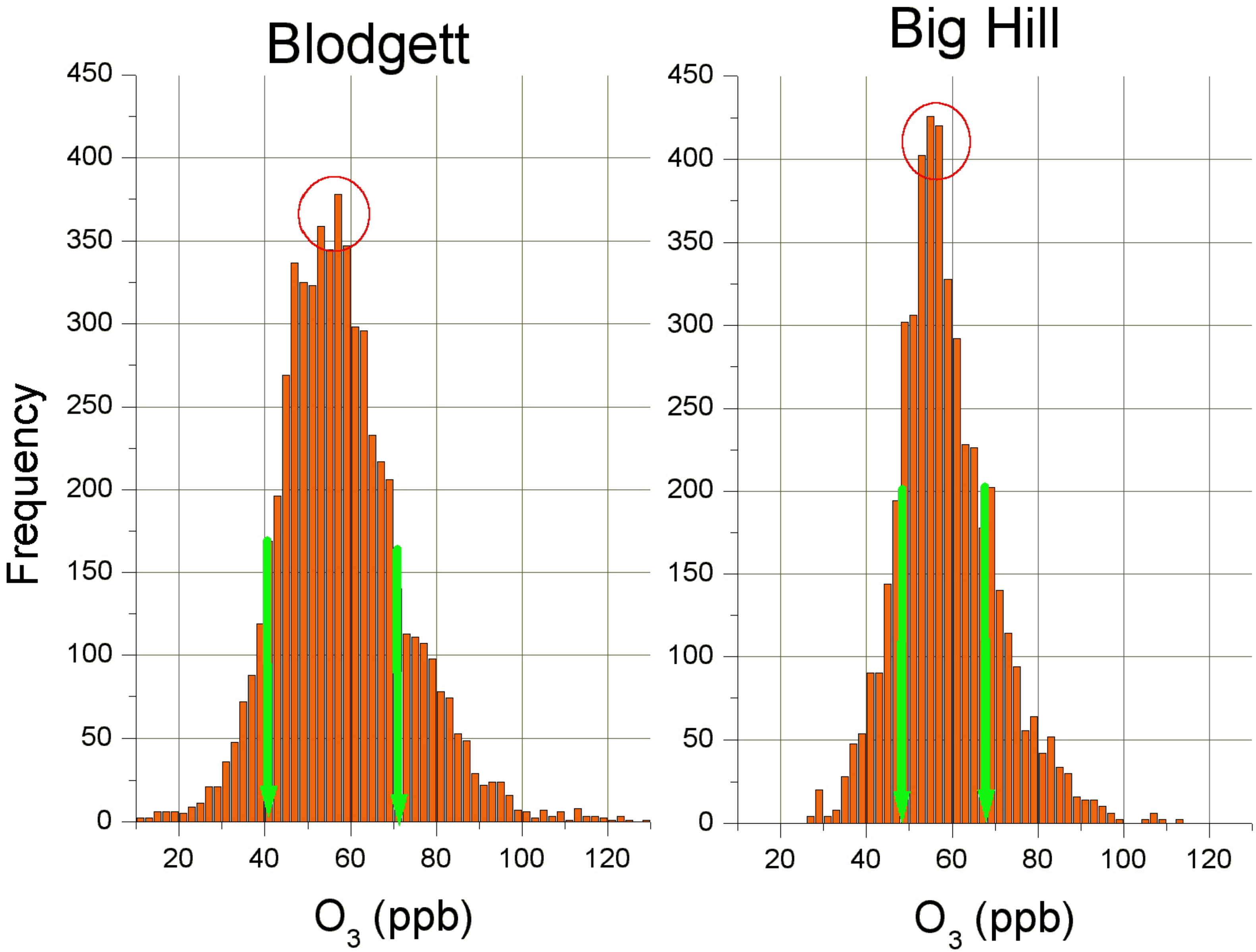
- Night

  Chemistry of NO_3 and deposition approaches zero.

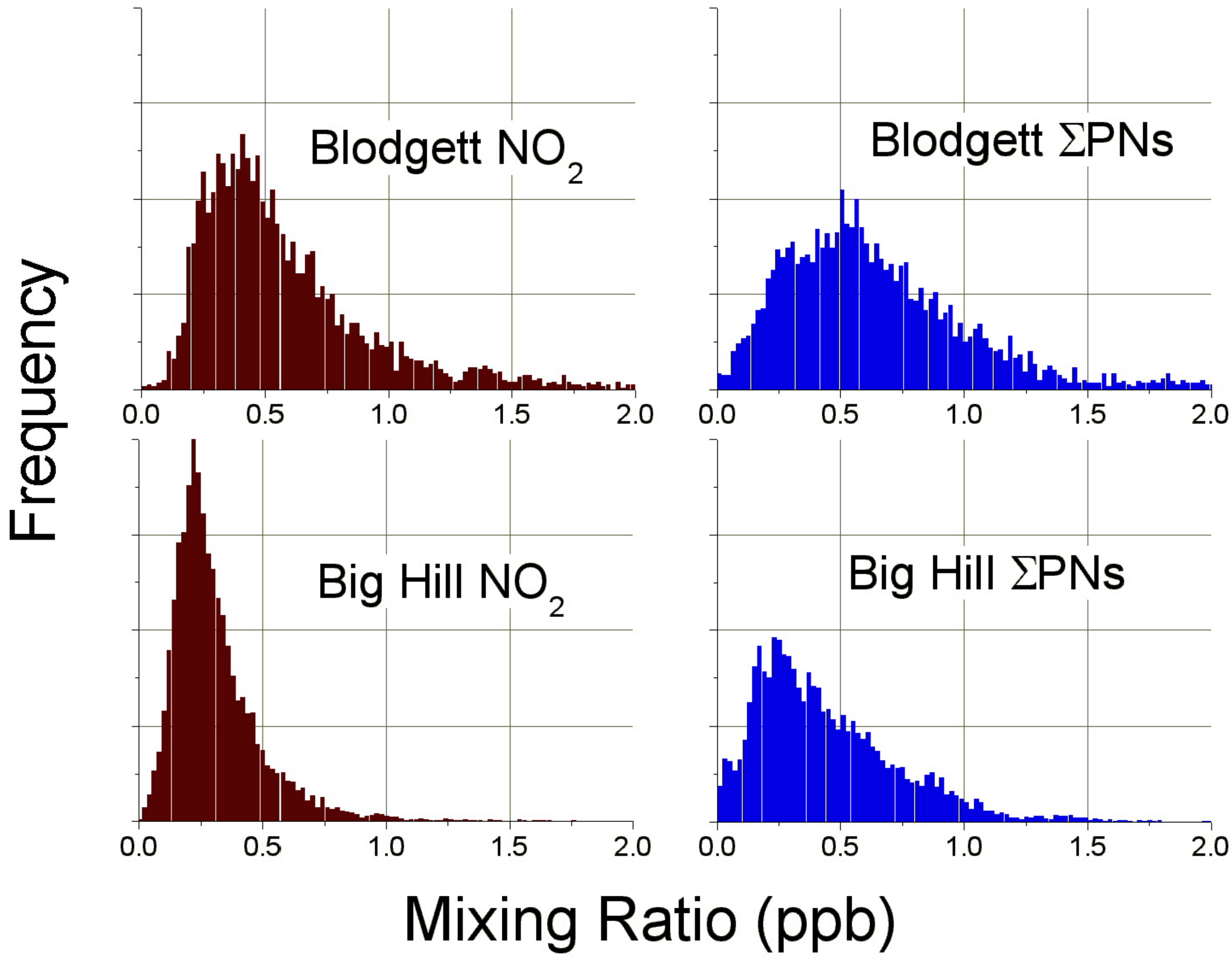
SANs ppb


BLOGDETT FOREST
GRANITE BAY
HOUSTON
1 .0
0 .8
0 .6
0 .4
0 .2
0 .0
0
4
8
1 2
1 6
2 0
2 4
H o u r o f D a y

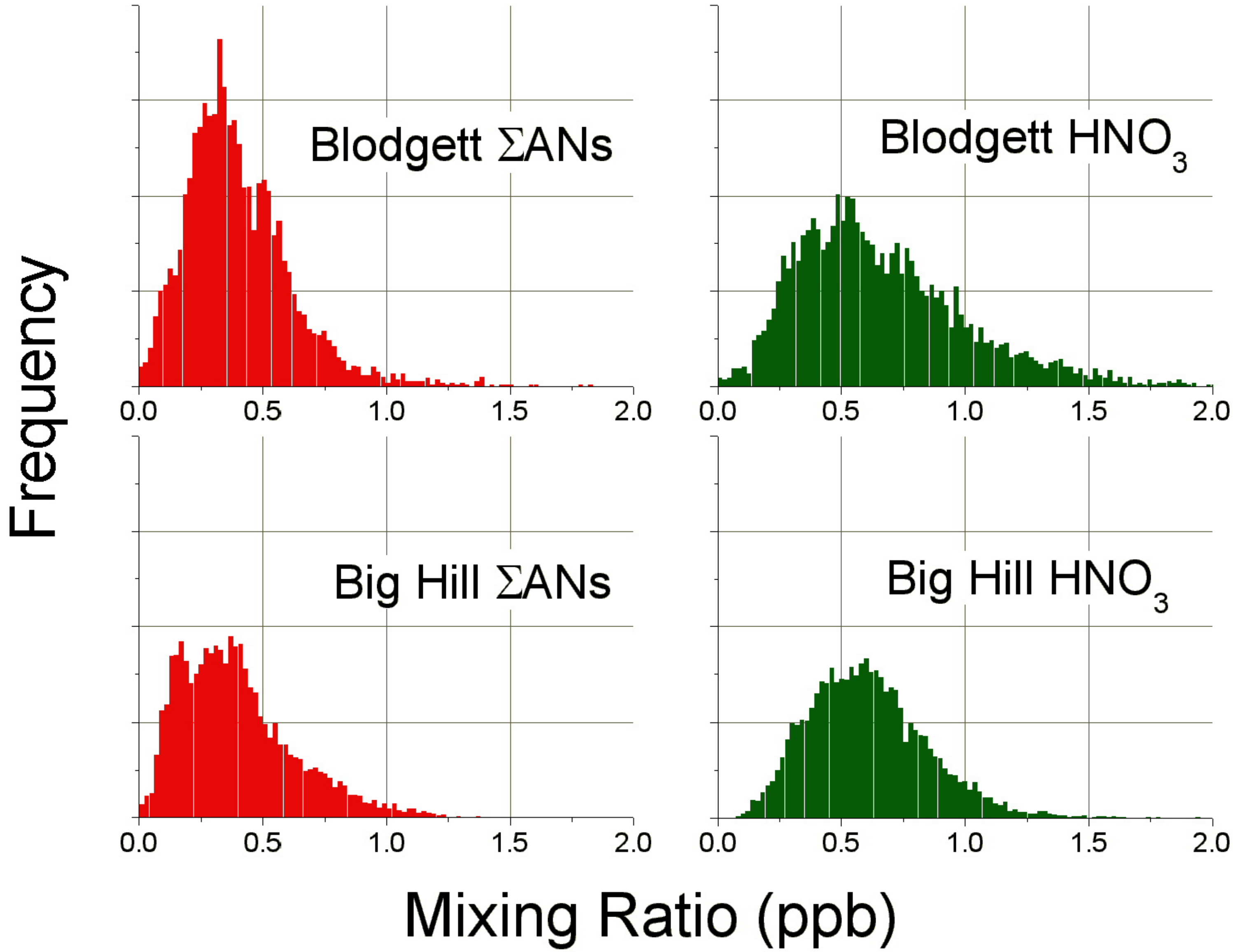
The observed variance of O_3 mixing ratios at Blodgett and Big Hill



The observed variance of NO_2 and ΣPN mixing ratios at Blodgett and Big Hill



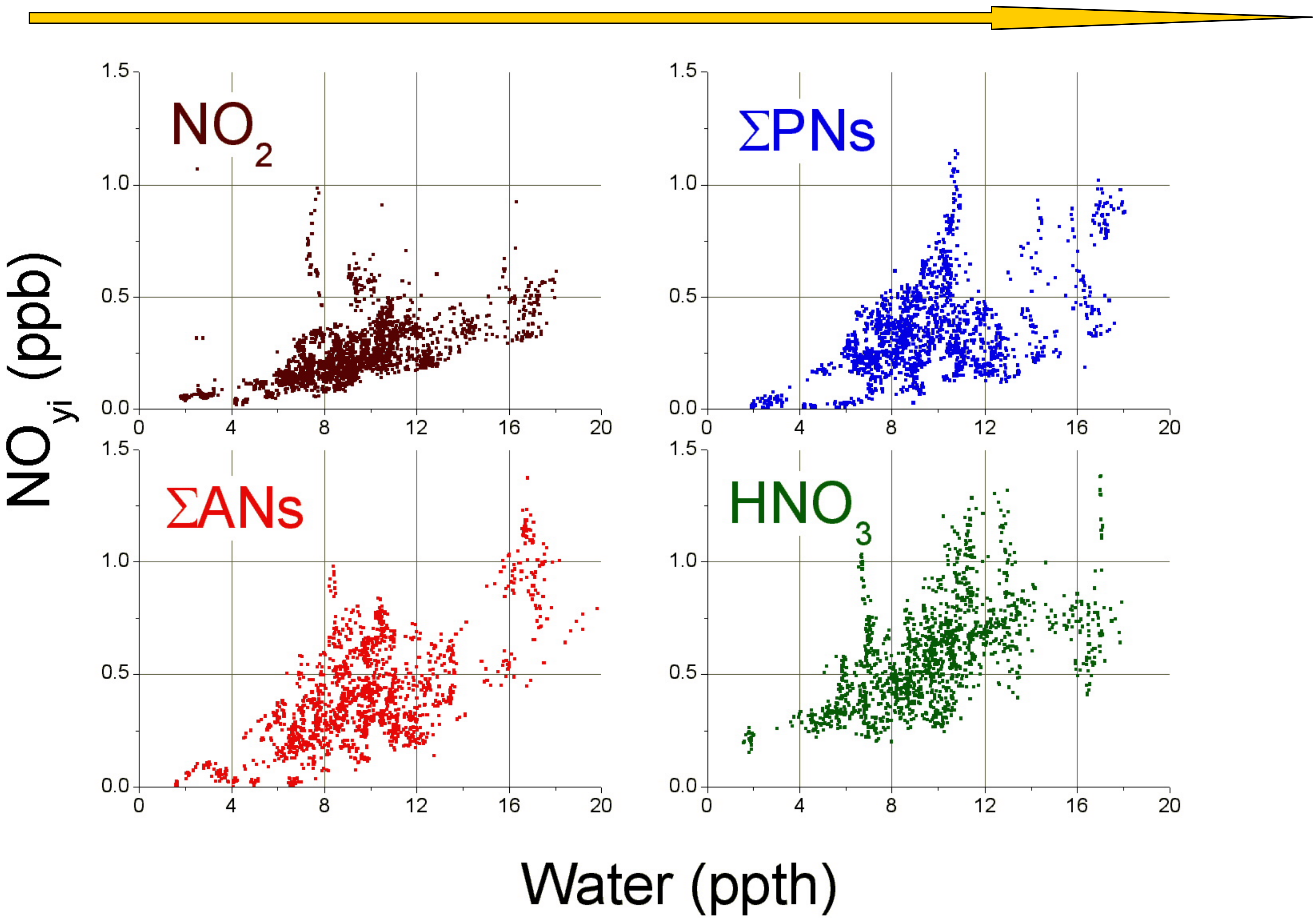
The observed variance of NO_2 and ΣPN mixing ratios at Blodgett and Big Hill



- The variance of the NO_{y_i} chemicals is proportional to the local NO_2 concentration.

- Extreme events are even less important at Big Hill than at Blodgett.

Correlations of water and NO_y at Big Hill (July '03) suggest mixing of air from the valley with the free troposphere



It may be possible to use these correlations and observations of water mixing ratio at other sites down wind of Big Hill to estimate potential transport fluxes.

- How far does ‘Sacramento plume’ travel in one day?
- How much dilution and oxidation occurs as the plume moves downwind?
- What do observations of NO_{yi} show?
- Summary and Implications?

Conclusions

- Transport from the west is an extremely small contribution to the NO_y in the air at Lake Tahoe on the daily time scale—factors that contribute to a large regional background that accumulates over multiple days of NO_y may contribute. The source of this background is not understood.

- During the day HNO_3 has a lifetime of about 3 hours and its mixing ratio is controlled by OH, NO_2 and deposition rates. Since OH is strongly buffered, local (within 3 hrs transport time) sources of NO_x and are the major atmospheric variable affecting HNO_3 dry deposition fluxes.

- We don't yet have a complete story explaining ΣPNs and ΣANs, but to the extent that they do deposit rapidly they are unlikely to be a source for N-transported into the basin.

- There is a wealth of high time resolution annual and multi-year data to assess chemistry and transport of nitrogen oxides along the western slopes of the Sierra.

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